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illustrated by*

AN ATLAS OF PHOTOMICROGRAPHS

by

C. F. POWELL

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Isotopic geochemistry of sulphur*

W. U. AULT† and J. L. KULP

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(Received 21 February 1958, and in revised form 4 September 1958)

Abstract—The isotopic composition of sulphur has been determined for a large number of specimens representing the important geochemical phases in which sulphur is present. The most significant process that causes sulphur isotopic fractionation is the reduction of dissolved sulphate by bacteria, although other processes such as distillation of volcanic emanations, oxidation-reduction of H_2S , SO_2 and S during volcanism and sulphide-sulphate equilibrium under magmatic or hydrothermal conditions can be locally important.

The new data are combined with earlier work in an attempt to define the range and average S^{32}/S^{34} ratio of the various sulphur-bearing phases of the crust. The most important averages are meteorites 22.21, ocean sulphate 21.76, mafic rocks 22.16, plutonic silicic rocks 22.13, hydrothermal sulphides 22.13 and sedimentary sulphide 22.49 and post-Cambrian evaporite sulphate 21.80. A material balance calculation of the sulphur isotopes in the crust, although subject to considerable uncertainties, points to an average crustal composition of sulphur heavier than that for meteorites.

No age effect is found for at least the last 2×10^9 years. Finally, a geochemical theory is described to account for the apparent distribution of sulphur isotopes in the lithosphere.

INTRODUCTION

SULPHUR is a major element in the earth, is the dominant non-metal in most ore deposits and shows a wide range in isotopic composition. Since the isotopic composition of sulphur in its various geologic settings is a result of its geochemical history, an understanding of the sulphur isotopic distribution and behaviour may place significant restrictions on theories of evolution of the crust and of ore deposits. It is the purpose of this paper to present some new data on sulphur isotopic distribution and to construct an adequate geochemical theory for the behaviour of sulphur.

Investigations in the distribution of sulphur isotopes in nature were pioneered by THODE and co-workers (THODE, 1949; THODE *et al.*, 1949; MACNAMARA and THODE, 1950; SZABO *et al.*, 1950; THODE *et al.*, 1951; MACNAMARA and THODE, 1951; MACNAMARA *et al.*, 1952; THODE and MACNAMARA, 1953; THODE *et al.*, 1953, and THODE *et al.*, 1954) who showed the large variation that exists, the characteristic range of certain phases and the importance of bacteria. TROFIMOV (1949) and MACNAMARA and THODE (1950) compared the isotopic composition of meteoritic and terrestrial sulphur. Since the isotopic ratio for troilite from meteorites was found to be remarkably constant and since it appeared then to be roughly similar to the median value for terrestrial sulphur, MACNAMARA and THODE suggested that initially, terrestrial sulphur was identical in isotopic content with meteoritic sulphur. NOETZLIN (1952) analysed native sulphur from volcanoes and explored the possible application of isotopic ratio studies to volcanology. THODE *et al.* (1954) and FEELY and KULP (1957) have shown that the native sulphur

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deposits associated with salt domes are of biogenic origin. Hydrogen sulphide-sulphate fractionation of as much as 4.8 per cent was observed in nature. A maximum of 2.7 per cent was obtained in the laboratory (FEELY and KULP, 1957) between sulphate and bacteria generated H_2S . The application of the sulphur isotopic variation to the origin of sulphide deposits was considered by KULP, AULT and FEELY (1956). BATEMAN and JENSEN (1956), KULP *et al.* (1956b), VINOGRADOV *et al.* (1956b, 1957) and JENSEN (1958) have reported measurements on a number of ore sulphides. VINOGRADOV *et al.* (1956a) investigated the isotopic composition of sulphur in sedimentary pyrite. SAKAI (1957) determined the $\text{S}^{34}/\text{S}^{32}$ ratios in various sulphur minerals of igneous origin and attempted to relate the present isotopic composition of oceanic sulphates to volcanic SO_2 . He also estimated formation temperatures for sulphates in hot springs, fumaroles and epithermal ore deposits in Japan from sulphide-sulphate equilibria and sulphur isotopic ratios.

Despite all of this work the adequate data for material balance calculation and for an examination of many geological processes were still not present. In the present investigation over 500 additional natural samples containing sulphur were subjected to isotopic assay. These, and the data from previous work at Lamont include the sulphur isotopic composition of: (1) the sulphate of ocean water, evaporites, salt domes, limestone and hydrothermal deposits; (2) sulphides of igneous, hydrothermal and meteoritic origin; (3) hydrogen sulphide, sulphur dioxide and sulphur from volcanic emanations; and (4) hydrogen sulphide and native sulphur from biogenic origin. They are used to assess or refine the mean, range and relative contribution of sulphur isotopes in certain categories of materials. An attempt is then made to obtain an isotopic material balance of sulphur. Other problems examined include the use of sulphur isotopes in indicating the origin of ore sulphide and the age effect. The results make possible a more complete understanding of the isotopic geochemistry of sulphur.

TECHNIQUES OF SAMPLE TREATMENT AND MEASUREMENT

A modified Consolidated Electrodynamics mass spectrometer model 401 ($2\frac{1}{2}$ in. radius stainless steel analyser in a 180° permanent magnetic field), dual collector was used to determine the $\text{S}^{32}/\text{S}^{34}$ ratio in SO_2 gas prepared from the sample. The sample and secondary standard (tank SO_2) bulbs were both attached to the gas manifold of the mass spectrometer and very small portions of each were alternately expanded into a 2 l. reservoir volume and allowed to flow into the ion source. Details of the analytical technique are described elsewhere (AULT, 1957).

The reproducibility of isotopic analysis was determined by repeated analyses of an SO_2 sample prepared from sulphate and compared with the lighter tank SO_2 standard over a period of 17 months. The forty analyses thus made gave a standard error of the mean of ± 0.01 per cent and a standard deviation of ± 0.06 per cent of the $\text{S}^{32}/\text{S}^{34}$ ratio. The variation on the same day was about as much as between different days. All samples in this work were run at least twice. Except in a few cases where the sample was small the error affixed to the $\text{S}^{32}/\text{S}^{34}$ ratio at the 95 per cent confidence level (2σ) is taken as ± 0.015 .

Many sulphides are intimately associated with carbonates but the CO_2 can be essentially separated from the SO_2 by differential freezing. It was found by a series of experiments that under the conditions used in this study the CO_2 impurity had no effect on the sulphur isotope ratio. Many samples were examined for other impurities but none were observed in the SO_2 mass range.

Sulphur isotope ratios on a few samples were determined on the m/e (50/48 + 49) spectrum

as well as the 66/64 + 65 spectrum. The excellent agreement confirmed the absence of contamination in the SO₂ region.

The primary standard was troilite from Cañon Diablo meteorite which was assumed to have the value $S^{32}/S^{34} = 22.21$ to permit ready comparison with the McMASTER work (MACNAMARA and THODE, 1950).

Isotopic ratios for the primary and secondary standards of this work are shown in Table 1 along with the National Bureau of Standards Isotope Reference sample no. 120 and the Noetzlin elemental sulphur standard. HULSTON and SHILTON (1958) report 22.23 for four analyses of N.B.S. no. 120. This may indicate that elemental sulphur presents problems as a standard. Elemental sulphur crystals in close proximity from Gulf Coast salt dome cores show considerable variation as does volcanic sulphur.

Table 1. A comparison of isotopic ratios for standards*

Description	Runs	S^{32}/S^{34}
<i>Troilite, Cañon Diablo (second, independently acquired specimen)</i>		
HT 1a†	(3)	22.20
HT 1b	(2)	22.21
<i>Standard tank SO₂ no. 1</i>		
HT 9a	(5)	22.21
HT 9b	(3)	22.24
HT 9c	(6)	22.22
HT 9d	(4)	22.23
HT 9e	(7)	22.22
HT 9f	(7)	22.22
HT 9g	(7)	22.22
	Average	$22.223 \pm 0.004^\ddagger$
<i>Standard tank SO₂ no. 2</i>	(14)	22.305 ± 0.004
<i>Nat. Bur. Std. isotope ref. sample no. 120</i>		
HN 18a	(3)	22.18
HN 18b	(5)	22.18
<i>Noetzlin Std., no. S.P. 73, San Carron commercial elemental sulphur</i>		
	(4)	22.15

* Based on assumed value $S^{32}/S^{34} = 22.210$ of first specimen of Cañon Diablo troilite.

† Small letters refer to separate chemical preparations or tank gas aliquots.

‡ Standard error on the mean.

S^{32}/S^{34} ratios have been reported as an abundance ratio relative to an assumed value for meteoritic sulphur. To obtain the ratio of sulphur isotopes from the relative signals obtained from the mass spectrometer the composition of ion species impinging on the collector must be evaluated. This calculation is given in detail elsewhere (AULT, 1957). The final working equations are:

$$(S^{34}/S^{32})_{\text{sample}} = 0.04482 + 0.0491 \left(\frac{R_{\text{sample}} - R_{\text{tank std. no. 2}}}{R_{\text{tank std. no. 2}}} \right) \quad (1)$$

$$\delta S^{34}_{\text{sample}} = 1091 \left(\frac{R_{\text{sample}} - R_{\text{tank std. no. 2}}}{R_{\text{tank std. no. 2}}} \right) - 4.41 \quad (2)$$

where the R 's refer to the mass spectrometer ratio measurement mass 66/mass 64 + mass 65.

For most specimens it was possible to separate clean sulphide or sulphate minerals with the aid of a magnifying glass. Some disseminated minerals were concentrated by means of shaking table and heavy liquids (tetrabromoethane for galena from carbonates, Clerici solution for galena, pyrite, chalcopyrite and barite). Pyrite from granite to gabbro rock types was concentrated by flotation methods using xanthate by OLAVI KOUVO at Rutgers University.

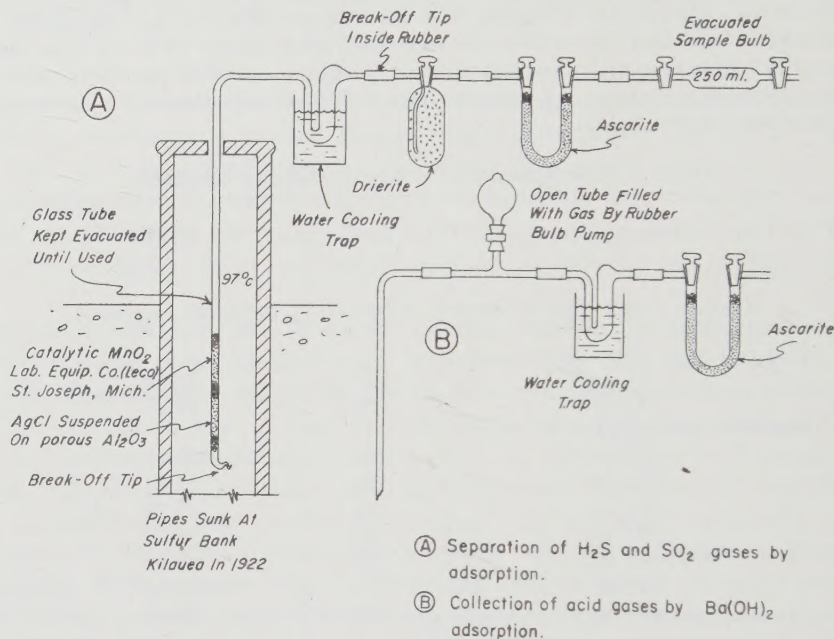


Fig. 1. Apparatus for the collection of volcanic fluids (designed by NAUGHTON).

Since acid leaching and also the xanthate separation might produce fractionation, a portion of the pyrite sample HP41 was allowed to react with dilute nitric acid for one minute and then washed. This was essentially the exposure that occurred during sample separation. Isotopic ratios of untreated and treated pyrite were identical, showing absence of detectable fractionation.

Sulphur dioxide gas was prepared from sulphides and sulphates in the usual manner (AULT, 1957).

The apparatus used by NAUGHTON of the University of Hawaii for the collection of volcanic fluids is shown diagrammatically in Fig. 1. Large quantities of fumarolic gases were pumped through system B. After cooling, the acid gases were adsorbed on ascarite. System A was an attempt to separate H₂S and SO₂ gases by differential adsorption onto AgCl and MnO₂, respectively, before they arrived at the surface and reacted to produce native sulphur and water. The MnO₂ and AgCl solids were placed directly in the SO₂ preparation system and roasted in oxygen at 700–750°C for 30 min. Gases adsorbed on Ba(OH)₂·8H₂O were released by acidification.

Sulphur dioxide was prepared from the sulphides in mafic igneous rocks by heating 150 g of crushed rock in oxygen at 1000°C for 1 hr after outgassing at 250–300°C for 20 min. The evolved H₂O was removed with P₂O₅ and the CO₂ separated from the SO₂ by differential freezing. Repeat combustions were made where necessary to obtain adequate quantities of SO₂.

Experiments on the reproducibility of sample preparation were reported by FEELY and KULP (1957). Additional experiments on the combustion of galena from one vial of finely-crushed pure galena over a period of 2 years under various conditions of combustion temperatures, combustion time, O₂ flow rate and SO₂ yield gave a standard deviation of ± 0.017 to the S³²/S³⁴ ratio.

The reproducibility of the combustion operation based on analyses of several types of sulphur mineral samples has shown that the deviation among all the preparations was no greater than

the reproducibility of the mass analysis despite great differences in combustion conditions and yields (AULT, 1957). Therefore it is concluded that fractionation during sample preparation is negligible, i.e. is less than ± 0.01 to the S^{32}/S^{34} ratio.

A good indication of the absence of fractionation in the reduction of sulphate samples is the very narrow range for all sea water sulphate samples (Table 4).

RESULTS

The samples and measurements of this study are summarized in Table 2 according to geographical locality and in Tables 3, 4 and 5. In some cases a more complete description and the original source of the sample is given elsewhere (AULT, 1957).

CAUSES OF ISOTOPIC VARIATIONS IN SULPHUR

The important cause or causes of isotopic fractionation of sulphur must be defined before the geochemical history can be deduced from the isotopic data. It is therefore necessary to consider physical, chemical and biological processes which may potentially be effective in producing isotopic variations in sulphur.

Diffusion is a possible mechanism for isotopic fractionation but examples in nature are difficult to find. SENFTLE and BRACKEN (1955) have discussed solid state diffusion "in which the solute diffuses through solid matrix, along grain boundaries or over surfaces" and liquid or solute diffusion in which the solute diffuses through "static fluid solutions held intergranularly in saturated rocks" as the only situation that can be important in geologic processes. They conclude that it is highly improbable that a large body exists in which a major constituent is isotopically enriched by diffusion processes but that it might be found in very small volumes.

SILVERMAN (1951) analysed the oxygen isotopic composition across the transition zone from gabbro to the intruding granophyre at Bayfield County, Wisconsin. He suggested that "a progressively decreasing assimilation of rocks low in O^{18} by a fluid high in O^{18} could account for the trend in isotopic ratios." While it may be shown from petrographic evidence that such assimilation was probably very limited, there was apparently much replacement in the transition zone. At the existing temperatures oxygen isotopic exchange alone might produce the observed O^{18} distribution. The slightly greater O^{18} content in the granophyre may indicate in part a metasedimentary source for some of the oxygen. This example does not appear to require diffusion to produce the result.

Isotopic fractionation by diffusion of the H_2S in water wells of Ontario, Canada (THODE *et al.*, 1949; THODE *et al.*, 1954) has been suggested by HOERING and MOORE, 1958. The wells from 150 ft gave H_2S lower in S^{34} than one from 300 ft. It was found, however, that the isotopic composition of the sulphate in the waters also was heavier with depth so that similar activity of sulphate-reducing bacteria would readily account for the observed results.

HOERING and MOORE (1958) also point to the variation in the relative abundance of the nitrogen isotopes in natural gases from the White Oak Gas Field of Arkansas as evidence of fractionation by diffusion. Since the isotopic variation over the field is irregular the structure cross-section, source and direction of flow need to be determined to substantiate the interpretation.

Table 2. New sulphur isotopic ratios of various minerals

Sample no.	Location	Mineral	Description	S^{32}/S^{34}	δS^{34} (‰)
North America					
Canada					
HPr 17	Huron Claim Area, Winnipeg River, SE Manitoba in SE cor. of Shatford Lake	Pyrrhotite	Sulphides associated with gabbro sills	22.15	+2.7
HPr 18	Huron Claim Area, Winnipeg River, SE Manitoba in SE cor. of Shatford Lake	Pyrrhotite	Sulphides associated with gabbro sills	22.16	+2.3
HP 48	NE shore Werner Lake	Pyrite	With chalcopyrite, pyrrhotite from sulphide-bearing quartzite	22.14	+3.2
HMo3	Westernmost of Three Found Claims, between Rennie and West Hawk Lake	Molybdenite	Associated with chalcopyrite from quartz-feldspar-biotite pegmatite	22.21	0.0
HP49	Westernmost of Three Found Claims, between Rennie and West Hawk Lake	Pyrite	Associated with HMo3	22.18	+1.4
HMo4	Easternmost of Three Found Claims, between Rennie and West Hawk Lake	Molybdenite	With chalcopyrite in quartz-feldspar-biotite pegmatite	22.18	+1.4
HP50	Easternmost of Three Found Claims, between Rennie and West Hawk Lake	Pyrite	Associated with HMo4	22.18	+1.4
HM20	Ontario, Kettle Point	Marcasite	Concretion in Huron shale (Devonian)	21.46	+3.8
HCh2	Mamainse Point, east shore of Lake Superior	Chalcocite	Mineralization filling zones of fracturing in the Keweenaw amygdaloidal basalt flows and pebble conglomerates	22.36	-6.8
HCh3	Mamainse Point, east shore of Lake Superior	Chalcocite	Mineralization filling zones of fracturing in the Keweenaw amygdaloidal basalt flows and pebble conglomerates	22.32	-5.0
United States					
HRS10	Boundary Co., Idaho	Pyrite	With pyrrhotite and chalcopyrite in isolated blebs and stringers in Purcell gabbroic sill	22.26	-2.2
HP42	Boulder, Montana	Pyrite	From diorite in Dandy Mine	22.15	+2.7
HP45	Boulder, Montana	Pyrite	From quartz monzonite	22.09	+5.4
HP46	Boulder, Montana	Pyrite	From monzonite	22.09	+5.4
HP43	Toston, Six Mile Creek, Montana	Pyrite	From gabbro	22.16	+2.3
HG250	South Dakota	Galena	With marcasite from Horseshoe Mine	22.08	+5.9
HM18	South Dakota	Marcasite	Associated with HG250	22.03	+8.1
HP44	Devil's Tower, Wyo.	Pyrite	Concentrated from phonolite	22.14	+3.2
HRS11	NW $\frac{1}{4}$, NW $\frac{1}{4}$ sec. 25, T61N, R12W, Lake Co., Minnesota	Chalcopyrite and pyrite	Disseminated in fresh Duluth gabbro	22.02	+7.5
HRS12	Lot 25, sec. 5, 61 N, 11 W, Lake Co., Minnesota	Chalcopyrite	With pyrite in Duluth gabbro	22.15	+1.7
HRS13	NE $\frac{1}{4}$, NE $\frac{1}{4}$, sec. 20, T60N, R12W, St. Louis Co., Minn.	Chalcopyrite	Masses up to several mm around twinned plagioclase crystals	22.03	+7.0
HRS6	Englewood, N.J.	Pyrite	Massive and cubic (1 mm crystals) among large pyroxene crystals in top of Palisades sill	22.05	+6.2
HP10	McAfee, N.J.	Pyrite	In weathering surface boulder	22.06	+6.8
HGy1	McAfee, N.J.	Gypsum (selenite)	Growing on pyrite-bearing boulder HP10	22.03	+8.1

Isotopic geochemistry of sulphur

Table 2—(contd.)

Sample no.	Location	Mineral	Description	S^{32}/S^{34}	δS^{34} (‰)
HP47	Adirondacks, N.Y. White Stone Farm	Pyrite	Concentrated from syenite	21.99	+9.9
HP57	Cortlandt, N.Y.	Pyrite	Disseminated in olivine-pyroxene rock	22.11	+4.5
HP58	Cortlandt, N.Y.	Pyrite	From emery quarry associated with garnet, biotite, and serpentine	21.78	+19.4
HP64	Welch Lake, Rockland Co., N.Y.	Pyrite	In weathering surface boulder	21.98	+10.4
HGy9	Welch Lake, Rockland Co., N.Y.	Gypsum (selenite)	Growing on pyrite-bearing boulder HP64	21.95	+11.7
HS48	Ellenville Mine, Ellenville, N.Y.	Sphalerite	With chalcopyrite	21.67	+24.3
HCp28	Ellenville Mine, Ellenville, N.Y.	Chalcopyrite		21.67	+24.3
HP63	Schoharie, N.Y.	Pyrite nodule	Baryman shale	21.58	+28.4
HP60	Cornwall, Penn.	Pyrite	Middle Hill	22.19	+0.9
HP61	Cornwall, Penn.	Pyrite	With hematite in shale	21.98	+10.4
HCp34	Cornwall, Penn.	Chalcopyrite	With pyrite Hp61	22.02	+8.6
HP62	Cornwall, Penn.	Pyrite	In magnetite, Big Hill	21.99	+9.9
HRS9	Broad Run Quarry, Fairfax Quadrangle, Virginia	Bornite and covellite	Irregular veinlike occurrence in Triassic diabase	22.21	0.0
South America					
Argentina					
HN7	Rio Atuel, Mendoza	Native sulphur	Volcano Overo	22.19	+0.9
Chile					
HN8	San Juan de la Vega, North Chile	Native sulphur	Supposedly volcanic	22.16	+2.3
HN10	San Juan de la Vega, North Chile	Native sulphur	Volcanic	22.39	-8.1
HN11	San Juan de la Vega, North Chile	Native sulphur	Volcanic (Azufre negro, black sulphur)	22.54	-14.9
HN12	San Juan de la Vega, North Chile	Native sulphur	Volcanic (Azufre amarillo mezclado con negro)	22.55	-15.3
HN13	San Juan de la Vega, North Chile	Native sulphur	Volcanic	22.21	0.0
Peru					
HP28	Cerro de Pasco	Pyrite	2300 ft level crystals	22.20	+0.4
HN4	Cerro de Pasco	Native sulphur	Interstitial between pyrite cubes HP 28	22.26	-2.3
HN5	Provincia Torata, Departamento de Tacna	Native sulphur	Volcan Yucamani	22.33	-5.4
HN16	Provincia Pacha, Departamento de Tacna	Native sulphur	Nevada (Volcan) de Huancané	22.51	-13.5
HN17	Provincia Pacha, Departamento de Tacna	Native sulphur	Nevada (Volcan) Achacolla	22.51	-13.5
HN6	Provincia Pacha, Departamento de Tacna	Native sulphur	Aucanquilcha Mine, Aucanquilcha Volcano	22.25	-1.8
HN9	Provincia Pacha, Departamento de Tacna	Native sulphur	Volcan Chupiquiña	22.33	-5.4
HN14	Roberto Claim, Departamento de Tacna	Native sulphur	Volcan Tutupaca highest 5670 m	22.32	-5.0
HN14r	Roberto Claim, Departamento de Tacna	Native sulphur	Recent, from base of Volcan Tutupaca	22.35	-6.3
HG275	Casapalca Mine	Galena	1200 ft level C-vein North with disseminated sphalerite, chalcopyrite, quartz, clay and carbonates, galena crystals up to 2 mm	22.22	-0.5

Table 2—(contd.)

Sample no.	Location	Mineral	Description	S ³² /S ³⁴	δS ³⁴ (‰)
HG276	Casapalca Mine	Galena	2700 ft level, massive coarse-grained vein of quartz, pyrite, galena and sphalerite. Pyrite intergrown	22.24	—1.4
HG277	San Cristobal Mine	Galena	170 ft level. Large tabular crystals of barite in galena sphalerite matrix. Manto-type orebody	22.12	+4.1
HG278	Cerro de Pasco Mine	Galena	600 ft level, 6203 stope. Veins and disseminations	22.25	—1.8
HG279	Marococha	Galena	In diorite. Pockets of galena, sphalerite and barite	22.23	—0.9
HN2	Hawaii Kilauea fissure of 1955 eruption	Native sulphur	Collected May 1956	22.57	—16.2
HN3	Kilauea fissure of 1955 eruption	Native sulphur	Collected May 1956	22.10	+5.0
HSo3	Sulphur Bank, sulphatanic fumarole brink of Kilauea Volcano Caldera	SO ₂ gas absorbed on catalytic MnO ₂	Collected 27 June 1956	22.23	—0.9
HGy16	Kilauea rift zone, 20 miles from crater, on Nii Farm, Puna, site of 1955 eruption	Gypsum crystals	Forming around sulphur cracks, also silica and native sulphur	22.46	—11.3
HN19	Kilauea rift zone, 20 miles from crater, on Nii Farm, Puna, site of 1955 eruption.	Native sulphur	Collected 29 June 1956	22.46	—11.3
HSo1	Kilauea rift zone, 20 miles from crater, on Nii Farm, Puna, site of 1955 eruption.	SO ₂ gas absorbed on Ba(OH) ₂	Collected 29 June 1956	22.39	—8.1
HG206	Africa Southern Rhodesia S.T. Mine near Bindura	Galena	Veins in arkosic metasediments	22.15	+2.7
HG207	Hardy Gold Mine, Darwin District	Galena	Vein in basement complex	22.14	+3.2
HP27	Hardy Gold Mine, Darwin District	Pyrite	With HG207	22.14	+3.2
HG209	Elba Mine, Wankie District	Galena	Vein in basement complex	22.24	—1.4
HG211	C.S.C. Mine, Marandellas District	Galena	W and Pb deposit in marble, pelitic metasediment, and Fe-quartzites	22.20	+0.6
HG217	Union of South Africa Rosetta Mine, Barberton, District	Galena	Quartz vein in Jamestown complex intrusive into Figtree schists	22.23	—0.9
HL1	Asia Badakshan Afghanistan	Pyrite	From lazurite	21.84	+16.7
HP37	Europe Finland Outokumpu	Pyrite	In black graphitic schist 100 m from ore "syngenetic with shales"	22.38	—7.7
HP59	Karhunsaaari	Pyrite	From sedimentary formation immediately above old gneiss disseminated in beds	22.65	—19.8
HP41	Urjala Sweden	Pyrite	Disseminated in granodiorite	22.24	—1.4
HG235	Falun, Langban	Galena	—	22.22	—0.5
HT4	Greenland Disco Island	Sulphur	From native iron as H ₂ S	22.23	—0.9

At Sterling Hill, New Jersey, there is a halo around the ore body in which the concentration of sphalerite increases from a few p.p.m. to several per cent and which may possibly have resulted from the diffusion of mineralizing solutions. Also in the Bonne Terre Mine, Mo., the consistent peripheral relationship of marcasite to galena appears to indicate a migration of the sulphur associated with iron just ahead of or beyond that which was associated with lead. Analyses of sulphur from these occurrences (AULT and KULP, 1959) give no evidence of isotopic fractionation by diffusion.

It is concluded that isotopic fractionation in nature is not produced to any large extent by diffusion processes.

There appears to be no evidence for appreciable fractionation of the sulphur isotopes during the transportation or deposition of hydrothermal sulphides (AULT and KULP, 1959). In a sufficiently oxidizing environment sulphide-sulphate equilibria may occur producing isotopic differences, but these situations represent a very small fraction of ore deposits.

Fractionation is also absent (i.e. less than ± 0.01 to the S^{32}/S^{34} ratio) during the normal crystallization of calcium sulphate from solution. This was shown by laboratory experiments (FEELY and KULP, 1957) and is supported by the identical sulphur isotopic composition of the dissolved and precipitated sulphate in the Laguna Madre, Texas, and the constancy of the S^{32}/S^{34} ratio in the anhydrite of the salt stocks all along the Gulf Coast (Table 5).

Two sets of samples from the New Jersey-New York Highlands area provided opportunity to look for isotopic fractionation due to oxidation during surface weathering. Selenite growing on the surface of pyrite-bearing boulders during the weathering process and the associated pyrite had the same sulphur isotopic composition within the experimental error (McAfee, N.J., and Lake Welch, N.Y., Table 2). Thus in surface oxidation of sulphides, as in the bacterial oxidation of native sulphur (FEELY and KULP, 1957), the process is essentially a quantitative one which does not allow isotopic fractionation. This is an important fact for it means that in the first chemical process (i.e. oxidation, solution and partial precipitation) which occurs after sulphur is brought from the mantle to the surface (as rock sulphide) the isotopic composition is not altered and this sulphur will initially enter the ocean as average crustal or mantle sulphur.

The equilibrium between H_2S and SO_2 existing in volcanic channels will shift in favour of H_2S at the lower vent temperatures (ELLIS, 1957). Two processes which occur at depth will tend to make the average of all emanations slightly lighter in sulphur isotopic composition than the primary source, i.e. the H_2S -metal sulphide equilibrium and the distillation process. The SO_2 forming in equilibrium with the H_2S will be enriched in S^{34} , further depleting the H_2S in this isotope. Native sulphur produced at volcanic vents might be assumed to have a highly variable composition, but on the average should be somewhat heavier than the H_2S from which it is formed. Both the oxidation of the H_2S to native sulphur and the subsequent oxidation of the sulphur by the oxygen of the air to SO_2 are not quantitative and may cause fractionation. Actually, therefore, the native sulphur which has a transitory existence at a fumarolic vent is constantly changing its isotopic composition. The range of composition in volcanic native

sulphur from the Andes and Hawaii (Table 2) is found to have an average value slightly higher than meteoritic sulphur and considerably higher than average crustal sulphur (discussed later). If the sampling is adequate these data suggest a significant fractionation between the H_2S and the sulphide in the magma phase. Even this phenomenon is not considered as a separate factor in the overall sulphur isotopic balance, since all the sulphur from both the gaseous and solid volcanic phases eventually ends up in the ocean.

The most important agent in isotopic fractionation of sulphur in the earth's crust appears to be sulphate-reducing bacteria as was first suggested by THODE *et al.* (1949). Experiments on the isotopic fractionation of the anaerobic sulphate-reducing bacteria in the laboratory by THODE *et al.* (1951), JONES *et al.* (1956) and FEELY and KULP (1957), have produced H_2S deficient in S^{34} by about 3 per cent. The greatest fractionation occurred with slow growth, limited food supply, an infinite reservoir of sulphate and low temperatures. THODE *et al.* (1954) and FEELY and KULP (1957) have observed sulphur isotopic fractionation in several geological situations, viz. salt lake in Africa, H_2S -bearing wells in Ontario and Gulf Coast salt domes that ranged from 3 to 6 per cent. The average bacterial fractionation in salt domes and lagoons where the largest material transfer has been observed is 2–3 per cent. Thus, although the initial anhydrite from the salt stock had a uniform isotopic composition of 21.85, the average composition of the sulphate in the calcite cap was 21.47 and the H_2S averaged 22.3.

The quantitative importance of bacterial reduction can be appreciated by realizing that millions of tons of anhydrite in each of the salt domes of the Gulf Coast have been converted to H_2S and sulphur by bacterial action (FEELY and KULP, 1957). Further, since the sulphur in the anhydrite has already undergone extensive fractionation from average terrestrial material by bacterial action in shallow ocean water, it would appear that the total variation of the sulphur isotopes in nature of about 11 per cent can essentially be accounted for by this phenomenon alone. Since these bacteria are active wherever there is sulphate ion, organic matter and a temperature less than 75°C , there are numerous places they can operate. It appears that the most important environment is in recent sediments during diagenesis, although many examples can be found of their activity in ancient porous strata associated with oil fields. Other significant locations are the bottom waters of restricted lagoons or seas and the surface of the ocean itself. Although the average fractionation between sulphate and resultant sulphide from bacterial reduction in a given site may only range from 2 to 3 per cent, the deposition of sedimentary sulphide in different locations than evaporite deposits (most of the sedimentary sulphate) makes separation and recycling possible.

DISTRIBUTION OF SULPHUR ISOTOPES IN NATURE

A compilation of available sulphur isotopic analyses of natural materials with the exceptions noted below are presented graphically in Fig. 2. The references for each type of sample used in this figure are given in the caption and will be used in all succeeding tables. Individual samples are plotted only for those types for which such information is meaningful in the discussion which follows. Averages obtained by weighting in various ways will be given in the evaluation of each source of sulphur.

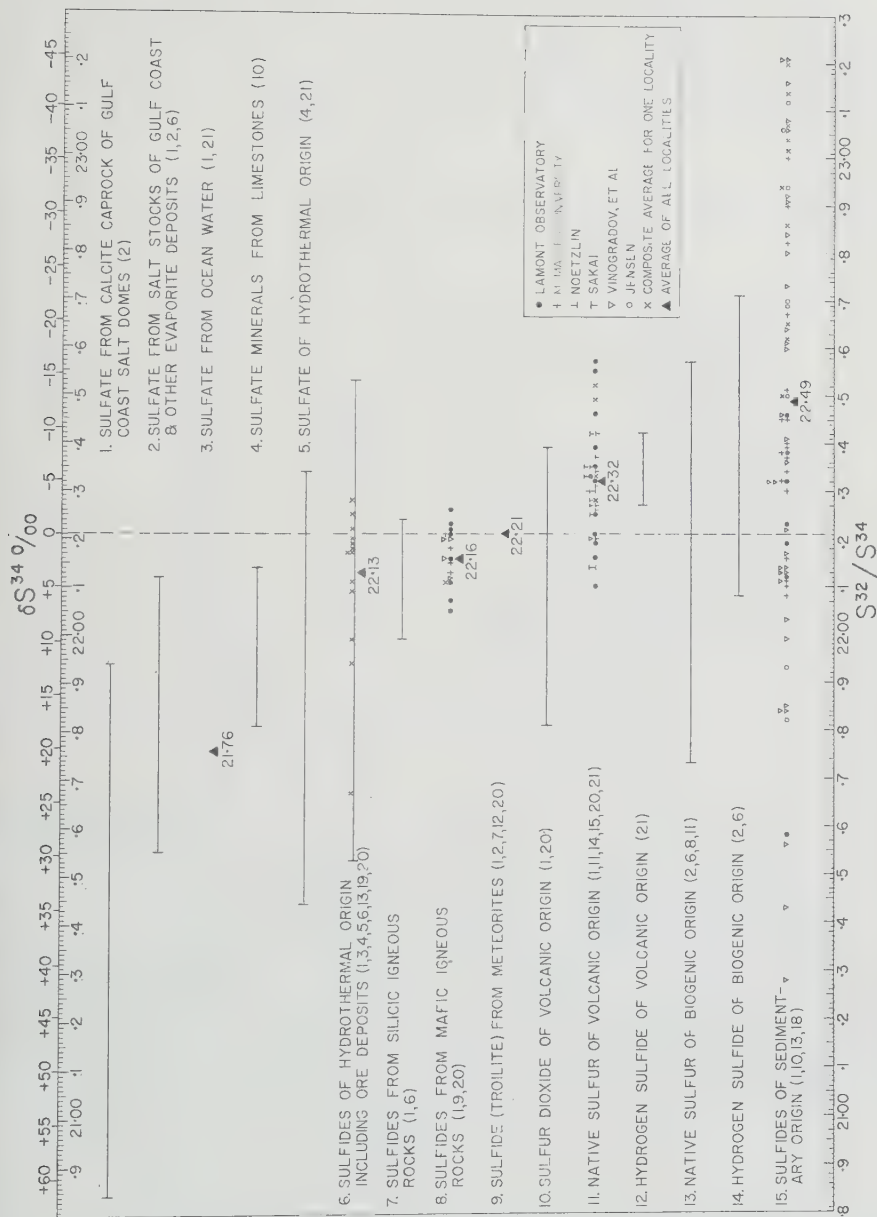


Fig. 2. Sulphur isotopic abundance in nature: (1) this paper; (2) FEELY and KULP (1957); (3) KULP *et al.* (1956); (4) AULT and KULP (1959); (5) ECKELMANN *et al.* (1959); (6) THODE *et al.* (1949); (7) MACNAMARA and THODE (1950); (8) MACNAMARA and THODE (1951); (9) MACNAMARA *et al.* (1952); (10) THODE *et al.* (1953); (11) THODE *et al.* (1954); (12) RANKAMA (1954), Ratios by McMASTER group; (13) KOUVO, personal communication (1956); Ratios by McMASTER group; (14) NOETZLIN (1952); (15) NOETZLIN, personal communication (1956); (16) JENSEN (1957); (17) JENSEN, 1958; (18) VINOGRADOV *et al.* (1956a); (19) VINOGRADOV, *et al.* (1956b); (20) VINOGRADOV *et al.* (1957); (21) SAKAI (1957).

Meteoritic sulphur

Five new analyses of the sulphur isotopic composition of meteoritic troilite are presented in Table 3. These are averaged with previous data of the MacMaster laboratory making a total of nine different siderites, one aerolite and one siderolite. Both laboratory groups have used Cañon Diablo as a primary standard so that the results are strictly comparable. Four analyses reported by TROFIMOV (1949) are omitted because they are all about a per cent low and there is no basis for inter-calibration.

Table 3. Sulphur isotopic ratios on troilite phase from meteorites

Type	Locality	Ref.*	S^{32}/S^{34}	δS^{34} (‰)
Siderite	Cañon Diablo Meteor crater, Ariz.	1, 2, 7	22.21†	0.0
Siderite	Xiquipileo, Mex.	1	22.20	+0.5
Siderite	Toluca, Mex.	12	22.23	-0.9
		1	22.21	0.0
Siderite	Richland, Tex.	1	22.23	-0.9
Siderite	Odessa, Tex.	1	22.18	+1.3
Siderite	Waterville, Douglas Co., Wash.	7	22.20	+0.5
Siderite	Duchesne Co., Utah	7	22.235	-1.2
Siderite	El Toba, Argentina	7	22.22	-0.5
Siderite	Goamus, S.W. Africa	12	22.22	-0.5
Aerolite	"Beenham", Union Co., N. Mex.	7	22.20	+0.5
Siderolite	Brenham, Kiowa Co., Kansas	7	22.23	-0.9
Average	(equal weight for each locality)		22.21	

* See Fig. 2.

† Average of twelve complete analyses, some on different portions of Cañon Diablo meteorite by different laboratories.

VINOGRADOV *et al.* (1956b) reported $S^{32}/S^{34} = 22.20$ from troilite from the gigantic iron meteorite Sikhota-alin. The same authors in their 1957 publication obtained identical values of $S^{32}/S^{34} = 22.20$ for nine stony meteorites and one achondrite using a technique which could measure the isotopic ratio to ± 0.01 per cent. In view of these results it appears that the isotopic composition of meteoritic sulphur is constant to at least ± 0.5 per cent and that the variations shown in Table 3 are probably experimental. For purposes of discussion the true value for meteorites will be arbitrarily assumed to be $S^{32}/S^{34} = 22.21$. The present measurements may be directly compared with the Russian work if the unit δS^{34} is used since both groups accept a meteorite primary standard.

Sulphate in ocean water

Twenty-five samples of sea water analysed in this investigation gave an average of 21.76 and were constant within the experimental error. These samples, assembled in Table 4, were widely distributed geographically and vertically. They included depth profiles from the Northern Pacific, a basin in the South Atlantic somewhat isolated by the Walvis Ridge, North Atlantic in both low and high latitudes on

Table 4. Sulphur isotopic ratios from sea water sulphate

Location		Depth (m)	S ³² /S ³⁴	δS ³⁴ (‰)
North Atlantic Basin				
Over Hudson Canyon Area				
39°20'N	71°45'W	Surface	21.78	+19.4
East of Florida				
25°05'N	69°58'W	40	21.77	+19.8
23°26'N	65°57'W	890	21.79	+18.9
23°26'N	66°09'W	4680	21.75	+20.7
Near connection to Newfoundland Basin				
38°20'N	43°50'W	910	21.76	+20.3
38°20'N	42°50'W	1830	21.77	+19.8
38°15'N	43°40'W	4970	21.78	+19.4
North Canary Basin				
East of Azores				
36°51'N	21°01'W	Surface	21.75	+20.7
36°50'N	21°20'W	910	21.76	+20.3
36°50'N	21°20'W	2740	21.78	+19.4
36°36'N	18°34'W	1820	21.75	+20.7
West of Straits of Gibraltar				
38°30'N	11°07'W	Surface	21.76	+20.3
36°56'N	14°00'W	180		
37°13'N	12°17'W	3660	21.76	+20.3
36°52'N	12°24'W	4390		
Cape Basin (South Atlantic)				
South of Walvis Ridge				
34°42'S	06°30'E	5100	21.78	+19.4
35°20'S	10°42'E	2195	21.76	+20.3
36°57'S	04°39'E	4300	21.75	+20.7
39°21'S	01°09'E	40	21.76	+20.3
North Pacific Basin*				
North of Hawaii				
39°56'N	158°39'W	0-92	21.75	+20.7
39°56'N	158°39'W	3925-4946	21.78	+19.4
47°01'N	164°56'W	3-113	21.77	+19.8
47°01'N	164°56'W	3764-4708	21.78	+19.4
"Standard sea water"†			21.75	+20.7
Gulf of Mexico				
27°24'N	89°25'W	1445	21.77	+19.8
25°24'N	89°51'W	2930	21.76	+20.3
Laguna Madre, Texas Coast				
Near Buoy Can No. 105 from inland waterway channel Salinity 63.8 ⁰ / ₀₀		3	21.78	+19.4
As above, over shallows, Salinity 62.5 ⁰ / ₀₀		Surface	21.76	+20.3
Average			21.76 ± 0.01 s.d.	

* Chinook Cruise, Baird Vessel, Scripps Oceanographic Institution.

† This sample by SAKAI (1957), all others present study.

either side of the mid-Atlantic Ridge, the Gulf of Mexico, and a lagoon bordering on the Gulf of Mexico.

Earlier measurements on sea water sulphate reported by FEELY and KULP (1957) gave the same average but are not given since the experimental technique was less precise. The Pacific Ocean sea water standard used by SAKAI (1957) is included.

The first ocean water sulphate analyses reported by SZABO *et al.* (1950) and MACNAMARA and THODE (1951) as averaging 21.80 with a 0.5 per cent variation are omitted since later THODE *et al.* (1953) indicated that subsequent measurements gave a much smaller spread. The new values have not as yet been reported.

In view of the careful attention given the problem of isotopic fractionation during chemical preparation and the many repeat analyses, it is concluded that the present-day ocean sulphate has a value of 21.76 ± 0.02 at the 95 per cent confidence level.

Sulphate in evaporite deposits and limestone

In North America there are a number of important evaporite horizons interspersed through the stratigraphic column. Data from some of these are summarized in Table 5. Apparently any given horizon in one basin contains sulphate of essentially constant isotopic composition (Cretaceous of Lafayette Co., Florida; Jurassic of Texas, Louisiana, Alabama; Middle Permian of Albany Co., Wyoming; Mississippian of Montana and Silurian of Michigan), probably that of the surrounding sea, but from one period to another (e.g. Upper to Lower Cretaceous, Jurassic to Permian, Pennsylvanian to Mississippian, Mississippian to Devonian to Silurian) or at least from one geologic setting to another, there may be differences up to 1 per cent from the present ocean value. An average for post-Cambrian time (21.80) was derived by weighting the average for each geologic period by the length of that period.

The differences among the various sulphate deposits can be ascribed to variation in the isotopic composition of the ocean reservoir or of a restricted basin or both. The Lower Cretaceous, Jurassic, Permian and Pennsylvanian deposits are clearly lighter, the Devonian and Silurian heavier and the Mississippian nearly the same compared with present ocean water sulphate. THODE's samples (1949) generally do not have adequate information to fix the stratigraphic horizon but the sample from Lockport, N.Y., $S^{32}/S^{34} = 21.69$, is almost surely Silurian in good agreement with the two samples reported in Table 5.

Gypsum in limestone is locally much more variable since it may either be produced by oxidation of sulphide after diagenesis or it may be attacked by bacteria resulting in a heavy residue. The range of the sulphates in limestone (Fig. 2) lies between the value for igneous rocks and the heavier sulphate deposits. Several of those measured by THODE *et al.* (1949) have been omitted due to the lack of geological data. The sulphur isotopic composition of the sulphate from the Jurassic Solenhofen limestone (THODE *et al.*, 1949) is the same as the Gulf Coast Jurassic but this is probably fortuitous since the older limestone sulphates measured by THODE *et al.* (1953) are all lighter than the evaporite sulphates.

The sulphur isotopic composition of a basin somewhat restricted from the ocean

Table 5. Sulphur isotopic ratios of extensive thick sulphate deposits of various ages in North America

Sample no.	Description	Location	S^{32}/S^{34}	δS^{34} (‰)
<i>Present</i>				
HW3-25	Sea water-sulphate. Average of 23 samples	(see Table 4)	21.76	+20.3
HW1,2	Sea water-sulphate. Average of 2 samples	Laguna Madre, Texas Coast	21.77	+19.8
HGy3	Gypsum. Forming in sea water	Laguna Madre, Texas Coast	21.76	+20.3
<i>Eocene</i>				
HA5	Anhydrite. Oldsmar fm.	Sec. 17, T24S, R25E, Oil Development Co. of Fla., no. 1, J. Ray Arnold, Lake Co., Fla. depth 2482 to 2515 ft	21.80	+18.5
<i>Cretaceous</i>				
HA17	Anhydrite	Sec. 25, T6S, R12E, Sun Oil Co., no. 1, P. C. Crapps, Lafayette Co., Fla., depth 1807 to 1817 ft	21.77	+19.8
HA18	Anhydrite	(Same as HA17) depth 1817 to 1827 ft	21.77	+19.8
HA14	Anhydrite	Sec. 20, T48S, R30E, Humble Oil and Refining Co., no. 1, Gulf Coast Realities, Collier Co., Fla., depth 8420 to 8430 ft	21.79	+18.9
HA15	Anhydrite	(Same as HA14) depth 10,290 to 10,300 ft	21.86	+15.8
HA3	Anhydrite	Sec. 25, T42S, R35E, Coastal Petrol Co., no. 1, J. Tiedtke and Wm. Shroeder, Glades Co, Fla., depth 11,259 ft	21.90	+14.0
<i>Lower Cretaceous</i>				
HA4	Anhydrite	Sec. 24, T59S, R40E, Sinclair Oil and Gas Co., no. 1, H. R. Williams, Monroe Co., Fla., depth 10,900 ft	21.92	+13.1
<i>Jurassic</i>				
FEELY and KULP (1957)	Anhydrite. Average of 21 samples from salt beds and plugs	Texas, Louisiana and Alabama	21.86	+15.7
<i>Mid-Permian</i>				
HGy11	Gypsum. Massive, white and granular. Embar fm.	Difficulty Creek, Carbon Co., Wyo.	21.99	+9.9
HG12	Gypsum. Embar fm.	T42N, R82W, Smith Creek, Shirley Mtns., Wyo.	21.95	+11.7
HGy14	Gypsum. Satanka fm.	Red Buttes Area, Albany Co., Wyo.	21.96	+11.3
HGy13	Gypsum. Phosphoria fm.	T48N, R90W, Wyo.	21.92	+13.1
<i>Permian</i>				
HGy15	Gypsum. White, porous and granular. Satanka fm.	Red Buttes Area, Albany Co., Wyo.	21.94	+12.2
<i>Pennsylvanian</i>				
FEELY and KULP (1957)	Anhydrite. Paradox fm.	Gen. Petrol. Corp., no. 1, Emery Co., Utah, depth 6485 ft	21.93	+12.7
<i>Mississippian</i>				
HGy10	Gypsum (Alabaster). Middle of Mich. Series, Alabaster quarry	Sec. 27, 21 N-7E, Iosco Co., Mich., depth 65 ft	21.84	+16.7
HA11	Anhydrite. Charles fm.	Sec. 24, T30N, R45E, Phillips Oil Co., Schultz no. 1, Valley Co., Mont., depth 5900 ft	21.83	+17.0
HA10	Anhydrite. Charles fm.	Sec. 13, T4N, R61E, Shell Oil Co., Little Beaver no. 1, Fallon Co., Mont., depth 6790 ft	21.84	+16.7
HA12	Anhydrite. Charles fm., white	Sec. 33, T10N, R58E, Fallon Co., Mont.	21.82	+17.6

Table 5.—(contd.)

Sample no.	Description	Location	S^{32}/S^{34}	δS^{34} (‰)
<i>Mississippian</i>				
HA13	Anhydrite. Dark gray stringers in core HA12	Sec. 33, T10N, R58E, Fallon Co., Mont.	21.82	+17.6
<i>Devonian</i>				
HA9	Anhydrite	Sec. 22, T15N, R54E, E.B. Reesor Vorhies, Dawson Co., Mont., depth 9399 ft	21.55	+29.7
<i>Silurian</i>				
HA7	Anhydrite	Sec. 25, 2N-7E, Sun Gidley no. 1, Oakland Co., Mich., depth 3802 ft	21.65	+25.2
HA6	Anhydrite. Basal Salina fm.	Approx. C.S.W. 31, 4N-15E, Casco Twp., Panhandle Eastern Brewer no. 1, St. Clair Co., Mich., depth 2625 ft	21.67	+24.3
THODE, et al. (1949)	Gypsum	Lockport, N.Y.	21.69	+23.4
Average* (Eocene-Silurian)			21.80	

* Obtained by weighting average for each period by length of period.

is determined by the balance of rates of influx of sea water and river water, precipitation of S^{2-} and SO_4^{2-} and bacteriological activity. If the influx carries average crustal sulphur, the S^{32}/S^{34} ratio of sulphate in a basin will be higher when the ratio of river influx to bacteriological activity is higher.

If restricted lagoons always had the same sulphur isotopic composition as the ocean, the observed differences from one horizon to another could be used for worldwide stratigraphic correlation.

There are two evidences that this may be the case: (a) sulphate from the sea water and gypsum being presently deposited in Laguna Madre, Texas Gulf Coast, has a sulphur isotopic composition identical to present day sea water average; (b) contemporaneous evaporite sulphates from widely separated localities appear to have a similar sulphur isotopic composition, e.g. Valley Co. Fallon Co., Montana and Iosco Co., Mich. (Mississippian); Oakland Co.-St. Clair Co., Mich. and Lockport, N.Y. (Silurian); Smith Creek-Red Buttes, Wyo. (Permian).

Isolated sulphate in limestone is subject to wide variation in bacteriological effects even though it may have been initially deposited in an open marine environment. Therefore this material cannot be used to determine the sulphur isotopic composition in the sulphate of palaeo-oceans. The absence of any pronounced overall trend in the evaporite or limestone sulphate from the Cambrian forward (Table 5) suggests that the sulphur isotopic composition in the ocean has not changed greatly or unidirectionally during this interval.

The change in isotopic ratio of sulphate-sulphur from Silurian to Mississippian as shown in Table 5 is about 1 per cent. This could reflect a diminution of bacteriological activity of about one-third. The critical question is whether the sulphur in the ocean reservoir may be changed in its isotopic composition in the time scale available. CLARKE (1924, 1954, pp. 118-119, 138) gives the annual contribution of sulphur by the rivers to the ocean of about 10^8 metric tons. Since the calculated

amount of sulphur in the sea is about 10^{15} metric tons, the average life of a sulphur atom in the ocean reservoirs would be about 10 million years. Thus if the bacteriological activity changed in a fraction of this time the observed difference between the Silurian and Mississippian evaporites can be explained as reflecting changes in the sulphur isotopic composition in the ocean reservoirs.

The possibility that this rate of turnover is too high due to recycled salts in river water, i.e. sulphate that is carried inland from the ocean by meteorologic processes and distributed on the land by precipitation, has been considered. Indirect calculations indicate that only between 7 and 12% of the sulphate is cyclic. However, JUNGE (1958) estimates from new data on precipitation in the United States that the world wide SO_4^{2-} concentration in precipitation on land is about 2.2 mg/l. This would calculate to 2.2×10^8 T of cyclic sulphate which is 2/3 of the total sulphate (3.3×10^8 T) given by Clarke (1924) as carried annually by the rivers to the sea. Therefore it appears safe to assume that the figure 10–30 m.y. for a turnover of sulphur in the ocean is reasonable and is short enough to offer an explanation for the observed changes within a geologic period or from one period to another.

If half of the amount of sulphate in the ocean were deposited as an evaporite bed it would amount to a deposit of only 1 km thick and about 1000 km square. This rapid turnover is not without parallel. According to McKELVEY *et al.* (1953) the amount of P_2O_5 in the Phosphoria formation in Wyoming–Idaho–Utah contains 1.7×10^{12} metric tons of P_2O_5 , or five times the total P_2O_5 presently in the oceans (0.23×10^{12} metric tons). Using the estimate 10^6 tons of P_2O_5 annually brought to the sea (KAZAKOV, 1950), a turnover of phosphorus could occur in 2 million years.

The alternate hypothesis is that the sulphur isotopic composition of a restricted marine evaporite basin is controlled by the competing factors of influx from rivers and ocean and bacteriological activity as well as the rate of deposition. In this case the sulphur isotopes could be an index of palaeoclimatic conditions.

Sulphate from calcite cap rock of the Gulf Coast

The average of these sulphates ($\text{S}^{32}/\text{S}^{34}$ about 21.5) is considerably lower than the evaporite sulphur in the anhydrite of the salt stocks from which the cap-rock sulphate is derived (Fig. 2). This cap-rock anhydrite is largely the residue after extensive bacterial fractionation. The light sulphates of this type are probably due to later oxidation of H_2S and native sulphur produced by the biogenic action. The average and range are probably similar to that which would be found in other salt dome cap-rock deposits scaled up or down by the $\text{S}^{32}/\text{S}^{34}$ ratio in the original evaporite horizon.

Sulphate in hydrothermal deposits

Hydrothermal sulphate samples from a number of mines and hot springs in Japan have been analysed by SAKAI (1957). Others from the Southeast Missouri Lead Belt, the Hanaoka Black Ore Deposit of Japan, and the Outokumpu deposit in Finland are reported by AULT and KULP (1959). The actual values are dependent on the initial isotope composition of the sulphide being oxidized, the

temperature of mineralization and the extent of equilibrium. The range of values observed are somewhat heavier than the ratios for the corresponding sulphides as expected.

Sulphides in mafic and ultramafic rocks

Primary sulphides associated with oceanic basalts, large basaltic and andesitic flows or diabase-gabbro intrusions on the continents would be most likely to show the primary sulphur isotope composition. If the origin of such rocks on the continents is sufficiently deep (i.e. if they originate below the Mohorovičić discontinuity)

Table 6. Sulphides from mafic igneous rocks

Description	Ref.*	No. samples averaged	S ³² /S ³⁴	δS ³⁴ (‰)
Pyrite, Palisades diabase, Triassic	1	1	22.05	+7.2
Bornite and covellite, Virginia diabase, Triassic	1	1	22.21	0
Pyrite, pyrrhotite and chalcopyrite				
Purcell gabbro sill, Idaho	1	1	22.26	-2.2
Sulphides, Duluth gabbro	1	3	22.07	+6.3
Pyrite, pyroxenite, Cortlandt, N.Y.	1	1	22.11	+4.5
Pyrite, gabbro, Six Mile Creek, Mont.	1	1	22.16	+2.3
Pyrrhotite, peridotite, Union, Me.	3	1	22.23	-0.9
Pyrrhotite, peridotite, Marie Pond, Me.	3	1	22.22	-0.4
Sulphides, Stillwater Complex, Mont.	9	3	22.15	+2.7
Sulphides, Sudbury, Ont.	1.9	12	22.11	+4.5
Sulphides, Nipissing diabase, Hecla Mine				
Cobalt, Ont.	9	1	22.18	+1.4
Sulphides, diabase, Ossion Twp., Ont.	9	1	22.21	0
Sulphides, Paracutin lava, Michoacán, Mex.	9	1	22.13	+3.6
Sulphides, Norilsk, gabbro diabase	20	13	22.12	+4.0
Sulphides, Kamchatka, basalt	20	1	22.16	+2.3
Sulphides, Aldan, pyroxenite	20	1	22.20	+0.4
Sulphides, Raiiz, dunite	20	1	22.20	+0.4
Average			22.16	

* See Fig. 2.

so that geosynclinal sediments do not contribute to the melt they should contain sulphides of uniform, primeval composition. Two factors could produce modification of this primeval ratio: (a) contamination with sulphur from rocks of the upper crust (particularly important in the case of intrusive bodies of small or moderate size) and (b) fractionation of the light isotope into volcanic emanations.

The available data on the isotopic composition of sulphides that appear clearly associated with mafic rocks are summarized in Table 6. Although the data are still very limited, the samples do represent a wide variety of occurrences. The average is clearly below that of meteorites. The samples of large bodies such as

the Duluth gabbro, Sudbury norite, Norilsk gabbro and Stillwater complex have a mean of about 22.12. The samples from smaller bodies simply tend to increase the spread.

It is difficult to estimate the effect of fractionation due to loss of the gaseous phase. As is seen from Fig. 2 native sulphur and H_2S from volcanic gases are clearly lighter than the meteorite average. This would tend to make the overall average $\text{S}^{32}/\text{S}^{34}$ for volcanic sulphur somewhat lighter than that obtained from the rock sulphide. Unfortunately, little quantitative information exists to determine

Table 7. Sulphides from plutonic silicic rocks including pegmatites

Description	Ref.*	No. samples averaged	$\text{S}^{32}/\text{S}^{34}$	δS^{34} (‰)
Boulder Batholith, Mont., (pyrite from diorite, qtz.-monzonite and monzonite)	1	3	22.11	+4.5
Devil's Tower, Wyo., pyrite in phonolite	1	1	22.14	+3.1
Otto Twp., Ont., sulphides in syenite	6	1	22.16	+2.3
Adirondacks, pyrite in syenite	1	1	21.99	+9.9
Urdala, Finland, granodiorite	1	1	22.24	-1.4
Southeastern Manitoba, pegmatites	1	7	22.17	+1.8
Falun, Langban, Sweden, pegmatite	1	1	22.22	-0.4
New England pegmatites (Welden, Red Hill, Plumbago and Newry, Me.; Fallen Quarry, Quincy, Mass.)	3	5	22.51	-13.4
Average (not including pegmatite)			22.13	

* See Fig. 2.

the relative quantities of sulphur in the two phases. From the isotopic material balance and the average $\text{S}^{32}/\text{S}^{34}$ ratio of plutonic rocks and hydrothermal sulphides, however, it would appear that the quantity of sulphur in the gaseous phase is a small fraction of the total.

Sulphides in pegmatites, granites, granodiorites and metamorphic rocks

The sulphur of the sulphides in these rocks presumably has come from some part of the crust which was originally sedimentary in character with the exceptions of differentiates in clearly igneous suites (e.g. Rockall granite, Stillwater granophyre) or granodiorites and latites from the deeper parts of the crust. Sulphides in pegmatites and metamorphic rocks may be expected to vary widely depending on the sulphur isotopic composition of the parent sediment. In many cases pegmatites appear to be derived locally or represent only a very small sampling of a metamorphic complex undergoing partial fusion. Large bodies of granite, particularly those that are clearly intrusive, might on the other hand represent a large enough volume element of the crust so that the sulphur it contained would have an isotopic composition of average less crustal material.

The limited number of analyses on this type of material are given in Table 7. The pegmatites, derived from the fraction of a metamorphic complex high in

original shale and, therefore containing sedimentary sulphide, tend to have light sulphur. The larger bodies of silicic rock, however, show an average S^{32}/S^{34} ratio of 22.13 which agrees with that of large mafic rock bodies within the error.

Sulphide in sedimentary rocks

This group consists of sulphides which occur as concretions and disseminated crystals in sedimentary rocks and which are apparently sedimentary and diagenetic in origin. The number of samples is still fairly limited but they do cover a good portion of post-Cambrian time (Table 8). Most of these samples come from shales but limestone and sandstone hosts are also included. The range of values is large, from $S^{32}/S^{34} = 21.3$ to 23.2. The raw average $S^{32}/S^{34} = 22.49$ lies well above the meteorite value. The greatest uncertainty in obtaining the crustal average for sedimentary sulphides lies in the assignment of weighting factors.

Sulphides of hydrothermal origin including ore deposits

Several hundred determinations of samples of sulphides from ore deposits and other obviously hydrothermal veins and disseminations have been made. Some of the new work is reported here (Table 9), the rest can be found elsewhere (KULP *et al.*, 1956a; AULT and KULP, 1959; ECKELMANN *et al.*, 1959).

All of the available data were used in plotting Fig. 2. It will be noted that the sulphur isotopic composition of these sulphides covers a large part of the range displayed by natural sulphur emphasizing the diverse rocks included in the origin of ore deposits.

The measurements on ore deposits where more than one sample has been analysed are summarized in Table 9. Although the sizes or types of ore bodies are not the same they appear to balance in a general way: thus one major Mississippi Valley District is heavy (SE Missouri) while another is light (Joplin). Although Friedensville represents small vein-like deposits so does Rapakivi, etc. Allowing equal weight for each district which is represented by five or more samples, the average for the hydrothermal sulphides is 22.12. If all of the localities are included for which less than five samples were measured, the average for the hydrothermal sulphides does not differ greatly from the average of the significant mining districts.

The distribution of the S^{32}/S^{34} ratio is quite sharp in some deposits but broad in others. In particular, where inhomogeneous extraction of sulphur from the shallow crust is involved (as possibly exemplified in the Mississippi Valley type ores, BATE *et al.*, in press), the sulphur isotopic composition varies widely. Where the sulphur- and metal-bearing hydrothermal solutions are derived from a magma chamber, the sulphur isotopes should be homogenized and the distribution of the S^{32}/S^{34} ratio sharp. The average from one deposit to another, however, may differ considerably depending on the sulphur isotopic content of the volume element of crust being melted. These observations point strongly to the crust as the source of virtually all mineralizing solutions.

SO₂, H₂S and native sulphur from volcanic gases

The hydrogen sulphide from Japanese volcanoes averages somewhat lighter in sulphur isotopic composition than meteorites and the volcanic sulphur dioxide from

Table 8. Sulphides in sedimentary rocks (roughly in order of age)

Description	Ref.*	S ³² /S ³⁴ †	δS ³⁴ (‰)
pre-Cambrian			
Pyrite in sediment, Karhunsaaari, Finland	1	22.65	-19.8
Pyrite in shale near ore, Outokumpu, Finland	1	22.32	-4.9
Pyrite syngenetic in shale, Outokumpu, Finland	1	22.38	-7.6
Pyrite from black schist, Outokumpu, Finland	13	22.45	-10.7
Pyrite from black schist, Outokumpu, Finland	13	22.39	-8.1
Pyrite from black schist, Outokumpu, Finland	13	22.40	-8.5
Concretion (Archean), McIntyre Mine, Porcupine, Ont.	10	22.08	+5.8
Pyrite in shale cleavages in Archean limestone, Pine Cone Lake, Ont.	3	22.18(2)†	+1.4
Marcasite nodules in shale, Pine Cone Lake, Ont.	3	22.19	+0.9
Pyrite from Bruce conglomerate, Bruce Mines, Palledean Island, Ont.	10	22.11	+4.5
Pyrite, Wateron Lakes, B.C.	10	22.10	+4.9
Pyrite from Keweenawan sandstone 1 mile N of Pte. Aux Mines, Lake Superior, Canada	10	22.16	+2.3
Cambrian			
Pyrite in clay, Krasnoye selo	18	22.32	-4.9
Pyrite in green clay, Krasnoye selo	18	22.41	-9.0
Ordovician-Silurian			
Pyrite from shale, Hudson River fm., Crawfish Creek, Cincinnati, Ohio	10	22.30	-4.0
Pyrite in clay interlayered with dolomite, Soviet bore hole, Lithuanian SSR	18	22.03	+8.0
Pyrite in shales, Caucasus	18	22.46	-11.2
Pyrite in grey clay, Chersky bore hole, NW of Russian Platform	18	22.61	-18.0
Pyrite from Lockport dolomite, Lockport, N.Y.	10	22.34	-5.8
Devonian			
Pyrite in calcareous shales Saxony	18	22.14	+3.1
Marcasite nodules, Huron shale, Kettle Point, Ont.	1	22.46	-11.2
Pyrite from Huron shale, Kettle Point Ont.	10	22.37(2)	-7.2
Pyrite nodule, Baryman shale, Schoharie, N.Y.	1	21.58	+28.3
Pyrite in clay interlayered with siltstone, Syzran	18	22.11	+4.5
Pyrite in sandstone with coal, Volga River, Samara Luka	18	22.14	+3.1
Pyrite in clay, Olkhovka, N slope of the Voronezh range of hills	18	21.28	+41.8
Concretion, Northern Urals	18	22.60	-17.5
Pseudomorphs in wood Rozhdestvensky bore hole, N slope of Voronezh range of hills	18	22.64	-19.3
Carboniferous			
Pyrite from upper Rundle fm., Banff, Alberta	10	22.32	-4.9
Pyrite in carbonaceous shale, Rakovka (the Kuybyshev Transvolga Region)	18	22.13	-3.5

Table 8 (*contd.*)

Description	Ref.*	S ³² /S ³⁴	δS ³⁴ (‰)
Pyrite in black siliceous silt shale, Aznakoyevo (Tatar SSR)	18	21.84	+16.6
Pyritized sandstone, Kuybyshev dist.	18	22.36	-6.7
Pseudomorphs in wood, Borovich, coal pit	18	22.80	-26.5
Pyrite from Bowland shale, Bolton Abbey, England	10	22.45	-10.7
Pyrite from pyritiferous shale, 6 miles W of Grand Falls, Newfoundland	10	22.51	-13.4
Pyrite from salty dolomite, Rocky Mtn. fm., S flank of Mt. Head, Alberta	10	22.38	-7.6
Permian			
Pyrite in clay, Kuybyshev dist.	18	21.85	+16.2
Pyrite in sandy clay in contact with petrol-asphalt sand Kuybyshev dist.	18	21.84	+16.6
Cardioceras concretion from Oxford clay, Warboys, England	10	22.82	-27.5
Triassic			
Sulphides from Chinle fm., Lucky Strike mine, San Rafael dist., Emery Co., Utah	17	22.50 (2)	-13.0
Sulphides from Chinle fm., Hidden Splendor mine, San Rafael dist., Emery Co., Utah	17	23.14 (5)	-42.0
Sulphides from Chinle fm., AEC no. 8 mine, Temple Mtn., San Rafael dist., Emery Co., Utah	17	22.86 (4)	-29.3
Sulphides from Chinle fm., Happy Jack mine, White Canyon dist., San Juan Co., Utah	17	23.04 (7)	-37.4
Sulphides from Chinle fm., Blue Lizard mine, White Canyon dist., San Juan Co., Utah	17	23.07 (4)	-38.6
Sulphides from Chinle fm., Gismo mine, White Canyon dist., San Juan Co., Utah	17	22.94	-32.9
Pyrite from Chinle fm., Mi Vida mine, Monticello dist., San Juan Co., Utah	17	23.20 (4)	-44.6
Pyrite from Chinle fm., Monument no. 2 mine, Monument Valley dist., Apache Co., Ariz.	17	22.94 (3)	-32.9
Pyrite in sand, Karagach bore hole, Black Sea region	18	22.17	+1.8
Pyrite in clay, Maykop	18	22.32	-4.9
Concretion of pyrite crystals on bone, Middle Kazakhstan	18	23.06	-38.3
Pyrite crystals on wood	18	23.16	-43.0
Jurassic			
Pyrite from Morrison fm., North Star mine, Uranium dist., Montrose Co., Colo.	17	22.70	-22.0
Pyrite from Morrison fm., Pitchfork mine, Gypsum Valley dist., San Miguel Co., Colo.	17	23.12	-41.0
Sulphides from Morrison fm., Little Eva mine, Thompsons dist., Grand Co., Utah	17	23.06	-38.3
Sulphides from Morrison fm., Mineral Joe mine, Bull Canyon dist., Montrose Co., Colo.	17	22.62 (2)	-18.5
Sulphides from Morrison fm., J. J. mine, Bull Canyon dist., Montrose Co., Colo.	17	22.65 (3)	-19.8

Table 8 (*contd.*)

Description	Ref.*	S ³² /S ³⁴	δS ³⁴ (‰)
Pyrite from Morrison fm., Woodrow Pipe mine, Grants dist., Valencia Co., N. Mex.	17	22.50	-13.0
Pyrite from Morrison fm., Shannon Oil Co., Claims Crook Co., Area, Wyo.	17	21.82	+17.5
Marcasite from Entrada fm., Garfield mine, Rifle dist., Garfield Co., Colo.	17	21.93	+12.5
Pyrite from Todilto limestone, F. O. Manol mine, Grants dist., Valencia Co., N. Mex.	17	22.69	-21.6
Pyrite in dark clay, B. Irgiz River	18	21.99	+9.8
Pyrite in clay, Kirov dist.	18	21.56	+29.2
Pyrite in clay, Novouzensk bore hole, Pricaspian Depression	18	22.08 (2)	+5.8
Concretion, Vologda dist.	18	22.84	-28.4
Concretion, Ryazan dist.	18	22.92	-32.0
Concretion in sand, Moscow dist. (Fili)	18	23.08	-39.3
Concretion in clay, Moscow dist. (Fili)	18	23.21	-45.0
Pseudomorphs in wood, Moscow dist. (Podolsk)	18	23.21	-45.0
Concretion, Moscow dist. (Podolsk)	18	22.91	-31.5
Cretaceous			
Pyrite in clay, Novouzensk bore hole	18	22.13	+3.5
Deshayesite, France	10	22.90	-31.1
Marcasite nodule from chalk, Cambridge, England	10	23.00 (2)	-35.3
Marcasite nodule from Austin chalk, Lancaster, Texas	10	22.67	-20.7
Eocene			
Sulphides from Wind River fm., Lucky Mc mine, Gas Hills dist., Fremont Co., Wyo.	17	23.02 (4)	-36.5
Average		22.49	

* See Fig. 2.

† Numbers in parentheses indicate the number of samples averaged to obtain this result.

Hawaiian and Japanese localities averages close to the meteorite value. The average of the volcanic native sulphur from both the South American Andes and Hawaii (Table 10) is also lighter than meteoritic sulphur but varies over a considerable range due to the complex reactions discussed above. More samples of this type are needed to compare the average sulphur isotopic composition in the volcanic gases with the associated lavas.

Native sulphur and H₂S of biogenic origin

These samples (Fig. 2) include the Gulf Coast salt domes, Ontario sulphur-bearing wells and sedimentary rock samples where bacterial action has been evident. The causes of the variations and the averages for different geological situations have been treated by FEELY and KULP (1957). The averages are

Table 9. Sulphides of hydrothermal origin (including ore deposits)

Description	Ref.*	No. samples averaged	S ³² /S ³⁴	δS ³⁴ (‰)
Rapakivi granite, Sakkijarvi, Finland	4	3	21.53	-14.3
Sottunga (granite), Finland	1	1	22.52	-13.9
Ellenville and Schwangunk Mines, N.Y.	4	7	21.67	+24.3
Southeast Missouri	4, 5	163	21.94	+12.1
Minnie Moore Mine, Bellevue, Idaho	3, 4	3	21.96	+11.2
Ill.-Wis., Pb-Zn Dist.	3, 4	17	21.99	+9.8
Cornwall, Pa.	4	4	22.05	+7.2
Horseshoe Mine, S.D.	4	2	22.06	+6.7
Ivigut, Greenland	3, 4	23	22.09	+5.4
Sudbury, Ontario	1, 9	12	22.11	+4.5
Sterling Hill and Franklin, N.J.	3, 4, 6	32	22.11	+4.5
Sunshine Mine, Idaho	4	2	22.12	+4.0
Pyrrhotite, Mary Mine, Ducktown, Tenn.	3	2	22.14	+3.1
Black Ore and other mineralization, Japan	4, 20	41	22.17	+1.8
Great Hope, Tucson and Little Pillsbury Mines, Leadville, Colo., Gilman, Colo.	3, 6	10	22.18	+1.4
Outokumpu, Finland	4, 13	9	22.19	+0.9
Peruvian Andes	4, 6	7	22.20	+0.4
South Africa	1	6	22.18	+1.4
Ill.-Ky. District	3	2	22.22	-0.4
Southwest U.S. (Ariz. and N. Mex.)	3, 4	26	22.25	-1.7
Parral, Chihuahua, Mex.	4	1	22.26	-2.2
Cu ore and sulfide mineralization in metamorphosed schists (Aijala, Orijarvi, Panjavaara, Attu Parainen and Pernaja)	4	5	22.25	-1.7
Joplin Missouri District	3	11	22.28	-3.0
Friedensville, Pa.	4	4	22.31	-4.5
Minas Carlota, Cuba	4	2	22.37	-7.2
Noril'sk, U.S.S.R.	20	10	22.12	+4.0
Buribaeusk, U.S.S.R.	19	5	22.13	+3.5
Other So. Urals, U.S.S.R.	19	4	22.16	+2.3
Central Ural, U.S.S.R.	19	17	22.19	+0.9
Aldan, U.S.S.R.	19	5	22.19	+0.9
Kola Peninsula, U.S.S.R.	19	1	22.36	-6.7
Korobkovsk, U.S.S.R.	19	1	22.25	-1.7
Koroganda, U.S.S.R.	19	1	22.12	+4.0
Maritime Province, U.S.S.R.	19	1	22.16	+2.3
Besshi, Japan	19	1	22.14	+3.1
Average for districts represented by five or more samples			22.12	
Average for all districts			22.14	

* See Fig. 2.

Table 10. Isotopic composition of volcanic exhalations

Description	Ref.*	S ³² /S ³⁴	δS ³⁴ (‰)
Sulphur dioxide			
Kilauea fissure, Puna, Hawaii, Mar. 1955	1	22.39	-8.1
Sulfur Bank, Kilauea, Hawaii, June 1956	1	22.23	-0.9
Fumarole No. 9101 and 9081, Mt. Showashinzan Hokkaido	21	22.33	-5.3
Fumarole 6, Mt. Shirane	21	21.81	+18.0
Native sulphur			
Kilauea fissure, Hawaii, May 1956	1	22.57	-16.1
Kilauea fissure, Hawaii, May 1956	1	22.10	+4.9
Kilauea fissure, Puna, Hawaii, June 1956	1	22.46	-11.2
Volcano Overo, Argentina	1	22.19	+0.9
San Juan de la Vega, Chile	1	22.16	+2.3
Volcan Tacora, Chile	1	22.39	-8.1
Volcan Chutinaz, Chile (average of two)	1	22.55	-15.2
Volcan Chutinaz, Chile	1	22.21	0
Cerro de Pasco, Peru	1, 15	22.28	-3.1
Volcan Yucumani, Peru	1, 15	22.33	-5.3
Volcan Nevada de Huancané, Peru	1, 15	22.49	-12.6
Volcan de Achacolla, Peru	1, 15	22.52	-14.0
Aucanquilcha Mine, Aucanquilcha Volcano, Peru	1	22.25	-1.7
Volcan Chupequina	1	22.33	-5.8
Volcan Tutupaca, Peru	1	22.32	-4.9
Volcan Tutupaca, Peru (recent)	1	22.35	-6.3
Nagusi Valley, Vanna Lava Is., New Hebrides	14	22.30	-4.0
Portes de l'Enfer, Pozzuoli, Italy	14	22.30	-4.0
Grande Soufrière de la Guadeloupe (4 samples) West Indies	14	22.14	+3.1
Fumarole 1, Tamagawa Hot Springs	21	22.26	-2.2
Fumarole 2, Tamagawa Hot Springs	21	22.35	-6.3
Fumarole 3, Tamagawa Hot Springs	21	22.27	-2.6
Fumarole 5, Mt. Yakeyama Springs	21	22.27	-2.6
Mt. Yakeyama (deposited in river water)	21	22.37	-7.2
Fumarole 6, Mt. Shirane	21	22.33	-5.3
"Yugama" the crater lake of Mt. Shirane	21	22.28	-3.1
Yonago Mine	21	22.34	-5.8
Mt. Asama, Nagano Prefecture (from the central crater)	21	22.14	+3.1
Shōzingawa Mine, Hokkaido	21	22.20	+0.4
Shozingawa Mine, Hokkaido	21	22.25	-1.7
Atosanupuri Mine, Hokkaido	21	22.42	-9.4
Manza Mine, Gumma Prefecture	21	22.31	-4.5
Ōwakudani, Hakone, Shizuoka Prefecture	21	22.42	-9.4
Zao Mine, Yamagata Prefecture	21	22.35	-6.3
Kunashir Island, Kuriles, Mendeleyev Volcano (average of 3)	20	22.20	+0.4
Italy, Stromboli (average of 2)	20	22.24	-1.4
Italy, Naples	20	22.21	0
Japan, Isan (average of 2)	20	22.21	0
Iceland, Krasuvik	20	22.24	-1.4
(average for native S)		(22.31)	

Table 10 (contd.)

Description	Ref.*	S ³² /S ³⁴	δS ³⁴ (‰)
Hydrogen sulphide			
Fumarole 1, Tamagawa, Hot Springs, Akita Prefecture	21	22.42	-9.4
Fumarole 2, Tamagawa, Hot Springs, Akita Prefecture	21	22.37	-7.2
Fumarole 3, Tamagawa, Hot Springs, Akita Prefecture	21	22.27	-2.6
Fumarole 4, Tamagawa, Hot Springs, Akita Prefecture	21	22.30	-4.0
Fumarole 5, Mt. Yakeyama, Akita Prefecture	21	22.29	-3.5
Fumarole 6, Mt. Shirane	21	22.40	-8.5
Fumarole 7, Okumanaza Hot Springs, Gumma Prefecture	21	22.29	-3.5
Average for volcanic S		22.33	

* See Fig. 2.

primarily a reflection of the basic raw material, i.e. the salt stock or sedimentary calcium sulphate from which the light sulphur is fractionated. In all cases the H₂S should be lighter than the native sulphur, an observation which is also consistent with the overall averages.

MATERIAL BALANCE OF SULPHUR ISOTOPES

Regardless of the early steps in planet accretion, the late high temperature stage in a reducing environment probably caused homogenization of the sulphur isotopes in the earth. Similar processes apparently produced the observed uniform sulphur isotope composition in meteorites. The sulphur isotope abundances in the earth and meteorites at the end of the high temperature stage need not have been identical depending on the relative degree of fractionation that may have occurred during the accretion process.

Initially erosion and sedimentation may have produced rocks with this same primary composition. Once sulphate-reducing bacteria appeared, however, fractionation began on the surface of the earth. It seems unlikely that the sulphur remaining now in the mantle can have an isotopic composition different from the primary value, owing to the high temperature and the absence of significant oxidation-reduction phenomena involving sulphur.

The thin basaltic crust over the oceans and the deeper mafic material under the continents probably have not been contaminated with sulphur that has reached the surface, so that these parts of lithosphere also should have the primary composition. The sum total of crustal and oceanic sulphur should also have an average equal to the primary value. Therefore, it should be possible to obtain an isotopic material balance for sulphur in the sulphide and sulphate minerals of the crust.

The parameters involved are the concentration of sulphur in each phase, the amount of each phase and the isotopic composition of the sulphur in that phase. The sulphur isotopic data, therefore, provide an independent method of testing the quantities of important phases of the lithosphere. Phases which obviously contribute a negligible amount of sulphur to the crust as a whole are omitted, such as salt dome sulphur in various chemical forms, hydrothermal sulphides and sulphates, volcanic native sulphur, biological sulphur and pegmatite sulphur. Surface lavas and volcanic emanations are transitory phases which are averaged

Table 11. Major source and isotopic composition of sulphur in continental and suboceanic crust

Material	Total mass $\times 10^{21}$ (g)	S (%)	Mass of S in phase $\times 10^{21}$ (g)	S^{32}/S^{34}
Meteorites	—	—	—	$22.21 \pm 0.01^*$
Mafic and plutonic rocks	22,192	0.15	33.3	22.13 ± 0.02
Shale	996	0.26	2.6	22.49 ± 0.05
Sandstone	104	0.05	0.05	22.49 ± 0.05
Evaporite sulphate	(4.25)	23.5	1.0	21.80 ± 0.02
Sea water sulphate	1,600	0.09	1.44	21.76 ± 0.01
Average crustal sulphur computed from sea water sulphate, evaporite sulphate and sedimentary sulphide				22.14

* Probable error on average.

† Including sulphate in connate water.

out in the ocean reservoir. Lavas are generally of deep-seated origin and may therefore be expected to contain primary (average crustal) sulphur and will only slightly affect the balance calculation. There are three major phases to consider: sedimentary and metasedimentary sulphide, ocean sulphate and sedimentary sulphate. Granite and granodiorite represent either large volumes of reconstituted sedimentary material with or without important additions from below, or are true differentiates of a more mafic magma. In either case they cannot be expected to deviate far from average crustal sulphur and thus may be omitted from the calculation. The limited data (Table 7) support this conclusion. Metamorphic rocks of high grade can also be considered in this category. Limestones are not important since they contribute a minor quantity of sulphur and contain both sedimentary sulphide and sulphate.

Table 11 gives the total mass of the important phases of the crust. The S^{32}/S^{34} ratios are derived as described above and the uncertainties represent the probable error on the average assuming a representative random sampling was obtained. The mafic and plutonic rocks are grouped together with a weighted average of 22.13 (see above). These and the meteorites are included only for comparison. It is assumed that sandstone has sulphur of the same isotopic composition as

shale and that deep-ocean sediments have that of average crustal sulphur, although neither are critical in the calculation due to the small quantity of sulphur involved. An estimate of the amount of shale is computed after POLDERVAART (1955), and the sulphur abundance in shale is taken as 0.26 per cent (CLARKE, 1924; from analyses by H. N. STOKES).

The mass of sulphur (after KOSSINNA, 1921; SVERDRUP *et al.*, 1942; KALLE, 1943; RUBEY, 1951, and POLDERVAART, 1955) and the isotopic composition of oceanic sulphate are known with much greater accuracy than any of the other phases. In order to compute the mass of sulphur in evaporite deposits (the only other important source of sulphate besides the oceans), the comprehensive tabulation and classification of sulphate deposits in North America by KRUMBEIN (1951) were used. Areas were estimated from the indicated extent of deposits. Those deposits less than 500 ft in thickness were neglected. Other thicknesses were divided by three to allow for interbedding with limestone and shale and by ten when interbedding was indicated as important. Adjustment was also made for salt composing part of the column. In order to obtain the world value it was assumed that the total sedimentary sulphate in the world geologic column is proportional to the total continental land area. With these estimates the mass of sulphur in evaporite deposits is of the same order of magnitude as that in the ocean but the uncertainty is rather large and may be conservative by a factor of 3 (SLOSS, 1957).

Both the isotopic composition and mass of sulphur in sedimentary sulphide are subject to considerable uncertainty. The quantities of sulphur contained in shale and evaporite deposits are sufficiently large to be critical in the material balance calculation. Nevertheless, if the isotopic ratios for each phase are weighted by the best estimate of the mass of sulphur in that phase, the average crustal S^{32}/S^{34} is computed to be 22.14.

Table 12 compares the estimates of the average isotopic composition of crustal sulphur with meteorite sulphur and with important phases of the crust. Included are extreme cases which assume (a) that the abundance of evaporite sulphur is actually three times the best estimate and (b) that the abundance of shale or its ratio difference (δ) should be increased by a factor of 1.5 and 2.

Since mafic rock (POLDERVAART, 1955) probably characterizes crustal sulphur, the material balance indicates that the best estimates of evaporite sulphate or sedimentary sulphides are probably not off by such large factors even though the average concentration of sulphur in shale is not too well known. The total mass of shale and the concentration of sulphur in shale can, of course, be varied inversely. Evidence on either one of these parameters alone cannot be obtained from the isotopic material balance calculation but as the latter becomes more closely defined through additional analytical work, this method becomes a powerful one to define the total mass of shale. Even at the present state of knowledge it seems unlikely that the sulphur concentration in shales can be in error by 50 per cent which suggests that POLDERVAART's (1955) estimate of the quantity of shales must be good to better than a factor of 2.

It appears from the results of Table 12 that the initial sulphur isotopic composition of the earth was heavier than that of the planet or planets from which the

Table 12. Comparison of various estimates of the average S^{32}/S^{34} ratio in the crust with meteoritic sulphur

Material	Assumptions	S^{32}/S^{34}
Meteorites		22.21
Mafic Rocks	Represents sample of mantle	22.16
	(or averaging large masses only)	22.12
Plutonic Rocks	Represents large sample of crust	22.13
Hydrothermal sulphides	Derived from representative set of crustal sites	22.12
Material balance of	(I) Best estimate of masses in each phase	22.14
sedimentary sulphide,	(II) Sedimentary sulphide best estimate,	22.05
evaporite and oceanic	maximum value for evaporite sulphate	
sulphate	(three times best estimate)	
	(III) Sedimentary sulphide mass or ratio	22.21
	difference increased by factor of 1.5,	
	evaporite sulphate best estimate	
	(IV) Sedimentary sulphide mass or ratio	22.14
	difference increased by factor of 2,	
	evaporite sulphate three times best	
	estimate	

meteorites formed. The material balance calculation gives support to this notion. It also provides independent evidence that the geochemical abundances of evaporite and shale deposits are approximately correct.

AGE EFFECT

As has been shown, bacteria produce virtually all of the isotope fractionation at the surface of the earth. THODE *et al.* (1953), from a limited sampling, suggested that sedimentary sulphate became lighter going back in time, whereas the sedimentary sulphide became heavier until the sulphur isotopic composition of these two phases appeared to converge about 800 million years ago. They inferred from these data that the bacteria (and possibly life) evolved at about this time.

There is little question but that such a phenomenon should be observed far enough back in time, i.e. to the origin of sulphate-reducing bacteria. The more extensive measurements now available, however, make it clear that there is no convergence of sedimentary sulphate or sulphide at 800 million years ago.

The sulphur isotopic composition of evaporite sulphate (Fig. 3) shows that there is no simple trend with age and in fact the earliest post-Cambrian deposits are even heavier than the present sea water. Unfortunately, no good samples of pre-Cambrian sedimentary sulphate have been obtained. Two samples of sulphate from pre-Cambrian limestone (probably about 1800 million years in age, pre-Huronian) reported by THODE are lighter (22.11, 21.99) than any of the evaporite deposits reported in Table 6 and sedimentary sulphate crystals in some Paleozoic limestone are also lighter than the sulphate from contemporaneous evaporite deposits. Therefore sulphate from limestone cannot be used to estimate the S^{32}/S^{34} ratio of ancient ocean water. VINOGRADOV *et al.* (1956a) showed that the

range of ratios for sedimentary sulphides and a few sulphates was nearly constant back at least to early Paleozoic and concluded that there was no age effect.

It is possible to carry the analysis of the age effect somewhat farther back in time with the available sulphide samples. Although the number of pre-Cambrian samples is still very limited, sedimentary sulphides from Outokumpu, Finland, which are at least 1800 million years old (Kuovo, private communication) show ratios as high as 22.38 to 22.45, and from Karhunsaaari a sedimentary sulphide of similar antiquity gives a S^{32}/S^{34} ratio of 22.65.

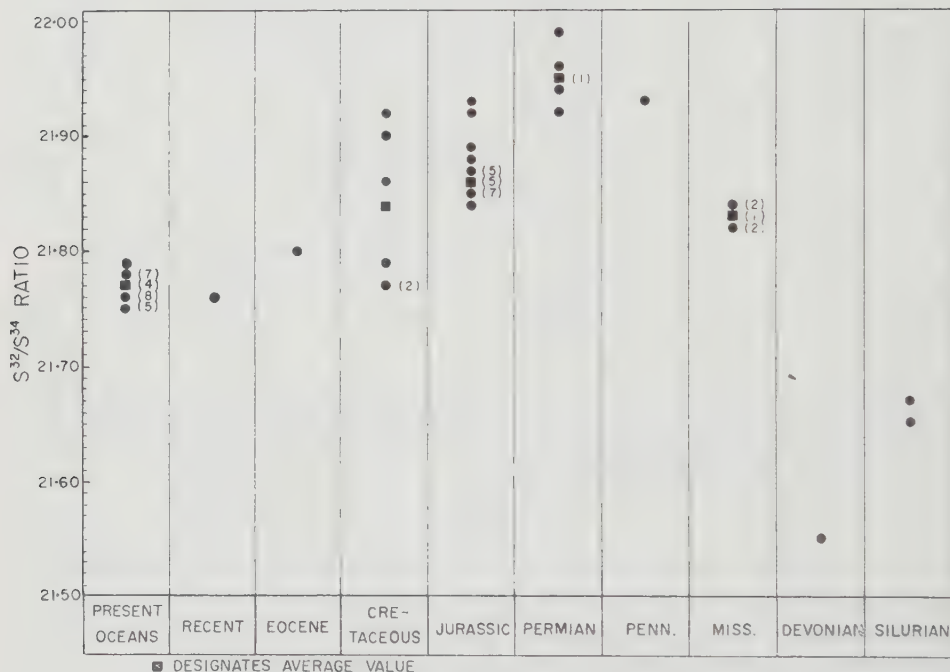


Fig. 3. S^{32}/S^{34} ratios in sulphate deposits of known age.

Another way of examining the sulphur isotopic fractionation as a function of time is to look for variations in the sulphur isotopic composition of hydrothermal sulphides, since such variations are presumably a reflection of their source environment, in the absence of hydrothermal sulphide-sulphate equilibria. The complex deposits at Franklin and Sterling Hill, N.J., (possibly 850 million years) show a very wide range of values. A number of the 2000 million years old galenas from Finland also show light sulphide (22.40, 22.52, AULT and KULP, 1959). On the other hand, the very ancient (~ 3000 million years) Southern Rhodesia and Union of South Africa ore samples give values fairly close to the average crust. This latter does not disprove the existence of highly fractionated sulphur in the crust at this time since these ore solutions could have picked up average sulphur from their sources. Nevertheless, they do represent a variety of deposits and their narrow range of S^{32}/S^{34} may indicate that at the time the source environment materials were at the earth's surface (3500–4000 million years ago) the bacterial fractionation was much less than now.

It is concluded that there is no simple age effect and apparently little change in the population of sulphate-reducing bacteria at least over the last 2000 million years. There is a suggestion that at 3500 million years ago the population was possibly a factor of 10 less.

GEOCHEMICAL THEORY

On the basis of the foregoing discussion, it is possible to construct a geochemical theory to account for the distribution of sulphur isotopes in nature.

The primeval cosmic isotopic ratio of S^{32}/S^{34} was 22.21 or higher, i.e. at least that found in present-day meteorites. During the course of earth accretion fractionation of the inert and lighter gases took place which caused some isotopic fractionation in the case of sulphur (and apparently also in carbon) such that the average S^{32}/S^{34} isotopic composition of the new planet earth was about 22.13. In the initial process of crustal differentiation the sulphur isotopic composition remained essentially unchanged. One possible exception would be the fractionation involved in the separation of H_2S in the gas phase from metallic sulphide in surface lavas. Evidence from Japan and Hawaii indicates that the sulphur of gaseous emanation is lighter than the rock sulphide counterpart. Further, any primary H_2S is fractionated on reaction with oxygen of the air to SO_2 and S, but these phases are transitory. The rock sulphide is largely converted to sulphate on weathering without detectable isotopic fractionation. In a geologically short time interval the volcanic emanations and the surface rock sulphides are oxidized and transported to the ocean as sulphate so that the average sulphur entering the ocean from this primary source will still have a S^{32}/S^{34} ratio of about 22.13.

Mantle material which is injected into the crust below the surface contains its sulphur with an isotopic S^{32}/S^{34} ratio of about 22.13. It may be slightly heavier if some of its gas phase has escaped to higher portions of the crust, or somewhat lighter or heavier if it has been contaminated with former sedimentary material.

This is in disagreement with VINOGRADOV *et al.* (1956b, 1957) who assume that average terrestrial sulphur is the same as meteoritic and then explain the heavy sulphur in high temperature sulphides and magmatic rocks as due to unknown processes of differentiation of crustal material.

The major process of fractionation takes place in the oceans, ocean margins and recent sediments (through diagenesis) where sulphate-reducing bacteria produce light sulphide and heavy sulphate. The actual S^{32}/S^{34} ratio in sulphate in ocean water is regulated by the following factors: (a) influx of sulphate from rivers (estimated world average is 22.13), (b) deposition of ocean sulphate and (c) bacterial activity. Since the ocean is mixed fairly rapidly (few hundred years) compared with the mean residence time of a sulphate ion (millions of years?) the bacteria are essentially operating on an infinite pool of sulphate ions of constant isotopic composition. The isotopic composition of locally produced sulphide, however, may vary by a large amount depending on temperature and food supply.

Shortly after the H_2S is produced it may react with dissolved iron to form iron sulphides. These may be compacted and recrystallized during diagenesis in the process of making shale and sandstone or remain more disseminated in ocean floor mud. The sulphur isotope composition can vary considerably from point to point

in these rocks with the S^{32}/S^{34} ratio tending to remain higher than 22.13. Limestone may incorporate some primary sulphate and in addition connate water in shale; sandstone and limestone will contain sulphate. This sulphate will be partially reduced during diagenesis depending on the food supply for the bacteria. Thus for example sulphate disappears in the brines of most formations as oil pools are approached. If burial is shallow and water circulation is high in limestones (generally low organic content) oxidation of syngenetic sulphide may occur yielding light sulphate.

Sulphur is not fractionated, at least at the ± 0.05 per cent level, during precipitation of evaporite sulphate. Hence, at least in the evaporite basin for a given time interval the S^{32}/S^{34} ratio should be constant and equal to that in the water from which it is formed. The competition of processes (a)–(c) noted above may cause gradual changes in the S^{32}/S^{34} ratio in dissolved sulphate in the oceans which will not be unidirectional with time.

During the metamorphic process under magmatic conditions sulphate tends to be reduced. Hence, at the source of origin of hydrothermal solutions the sulphide will have an isotopic composition that will reflect the relative contributions from the sulphur originally present in the sedimentary sulphide and sulphate of the environment. If homogenization of a large volume of the crust takes place such as in the formation of a true magma, the sulphur isotopic composition of the hydrothermal solution emanating from the volume should be quite uniform. If the volume element is large enough the S^{32}/S^{34} ratio in such solutions will approach the average for the entire crust or mantle. If the magma chamber is more restricted the S^{32}/S^{34} ratio will still be relatively constant but from one chamber to another may vary greatly from sulphur that is quite heavy to that which is quite light.

Pegmatite sulphide will have the S^{32}/S^{34} ratio of its immediate source environment. Since this presumably is largely arkose and shale originally it is not surprising that the sulphur in pegmatites is generally light.

When these second generation deposits or rocks are brought to the surface the sulphur is oxidized to sulphate like that of lavas and contributes the crustal average S^{32}/S^{34} ratio to the rivers, and hence the oceans, to renew the cycle. This overall process will not allow for the bacteria to cause greater and greater total fractionation with time. Rather the ocean level has fluctuated around a mean depending largely on bacterial productivity since sulphate-reducing bacteria became widespread.

CONCLUSIONS

(1) The S^{32}/S^{34} ratio of sulphur in meteorites is constant to within about ± 0.05 per cent. This S^{32}/S^{34} ratio is assigned the value of 22.21 and is used as a primary standard.

(2) Oceanic sulphate including the Gulf of Mexico and restricted Laguna Madre is also uniform within the experimental error giving $S^{32}/S^{34} = 21.76$.

(3) Evaporite sulphate represents the dissolved sulphate in the water of its basin of precipitation. The water of these restricted basins has been both heavier and lighter with respect to sulphur isotopes than present-day sea water, reflecting the competition of influx from rivers and oceans, deposition and bacteriological activity. Within a particular bed, however, the sulphur isotopic composition

appears constant over large areas and hence may be quite useful for stratigraphic correlation. An alternative use may be as an index for palaeo-climatic conditions. The values range from 21.55 to 21.99 with a weighted post-Cambrian average of 21.80.

(4) The largest local fractionation is that observed in salt dome caprock where active bacteriological activity can produce very heavy residual sulphate.

(5) Sulphate in limestone is probably produced in two ways, by initial deposition and by the oxidation of diagenetic sulphide. Hence, it varies considerably in sulphur isotopic composition.

(6) Sedimentary sulphide has an average isotopic composition of 22.49 based on a small number of samples.

(7) Basaltic rocks have an average S^{32}/S^{34} ratio of 22.12 if only the larger masses are considered. Smaller bodies are more readily contaminated by the rock through which they pass and come to rest. Granitic rocks show an average S^{32}/S^{34} ratio of 22.13. Pegmatites show a wide range and in general are light reflecting their local origin from metamorphosed shales.

(8) The oxidation of rock sulphide to sulphate in the weathering process does not cause detectable isotopic fractionation.

(9) The dominant process of sulphur isotopic fractionation is the action of sulphate-reducing bacteria in the ocean. This produces variable light sulphide in sediments. There is no simple age effect back to 2000 million years ago, hence the sulphate-reducing bacteria are much older than this.

(10) The bacteria cannot cause a continuously larger total fractionation since the sedimentary rocks on erosion yield all of the sulphur isotopes, so that the average sulphur entering the ocean should remain at about 22.13.

(11) Isotopic fractionation occurs at reduced temperatures in the vents of volcanoes between the gaseous and solid phases H_2S , S and SO_2 .

(12) Four lines of evidence suggest that the average isotopic composition of the earth, mantle and crust is 22.13 instead of the 22.21 of meteorites. These are the average isotopic compositions of sulphur in igneous mafic rocks (22.12), granitic plutonic rocks (22.13), hydrothermal sulphides (22.12) and the isotopic material balance calculated for all sedimentary sulphate and sulphide (22.14).

(13) The range in the average sulphur isotopic composition of ore deposits indicate a crustal origin for virtually all hydrothermal solutions. Uniform sulphur isotopes in a given deposit suggest magmatic activity which has homogenized the sulphur prior to intrusion, whereas large differences indicate inhomogeneous extraction such as in the case of the Mississippi Valley type deposits.

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REFERENCES

- AULT W. U. (1957) Unpublished Ph. D. Dissertation, Lamont Geological Observatory, Columbia University, N.Y.
- AULT W. U. and KULP J. L. (1959) Sulfur isotopes and ore deposits. *Econ. Geol.* In press.
- BATE G. L., GAST P. W., KULP J. L., MILLER D. S. and AULT W. U. (1959) Lead isotope abundances in lead minerals. *Trans. Amer. Geophys. Un.* In press.
- BATEMAN A. M. and JENSEN M. L. (1956) Notes on the origin of the Rhodesian copper deposits: Isotope composition of the sulfides. *Econ. Geol.* **51**, 555-564.
- CLARKE F. W. (1924) *The Date of Geochemistry* (5th Ed., 1954). *Bull. U.S. Geol. Surv.* 770.
- ECKELMANN F. D., KULP J. L., BROWN J. S., SNYDER F. and AULT W. U. (1959) Lead and sulfur isotopes and the history of mineralization in Southeast Missouri. *Bull. Geol. Soc. Amer.* In press.
- ELLIS A. J. (1957) Chemical equilibrium in magmatic gases. *Amer. J. Sci.* **255**, 416-431.
- FEELY H. W. and KULP J. L. (1957) The origin of Gulf Coast salt dome sulfur deposits. *Amer. Assoc. Pet. Geol.* **41**, 1802-1853.
- HOERING T. C. and MOORE H. E. (1958) The isotopic composition of the nitrogen in natural gases and associated crude oils. *Geochim. et Cosmoch. Acta* **13**, 225-232.
- HULSTON J. R. and SHILTON B. W. (1958) Sulfur isotopic variations in nature. Part 4—Measurement of sulfur isotopic ratio by mass spectrometry. *New Zealand J. Sci.* **1**, 91-102.
- JENSEN M. L. (1957) Sulfur isotopes and mineral paragenesis. *Econ. Geol.* **52**, 269-281.
- JENSEN M. L. (1958) Sulfur isotopes and the origin of sandstone type uranium deposits. *Econ. Geol.* **53**, 598-616.
- JONES G. E., STARKEY R. L., FEELY H. W. and KULP J. L. (1956) Biological origin of native sulfur in salt domes of Texas and Louisiana. *Science* **123**, 1124-1125.
- JUNGE C. E. (1958) Sulphur budget in the atmosphere. Paper given at annual meeting of American Geophysical Union, Washington, May 1958.
- KALLE K. (1943) *Der Stoffhaushalt des Meeres. Probleme der kosmischen Physik* p. 23. Leipzig.
- KAZAKOV A. V. (1950) Fluorapatite-system equilibria under conditions of formation of sedimentary rocks. *Akad. Nauk SSSR Trud. Inst. Geol. Nauk Vyp.* **114**, Geol. Ser., No. 40, 1-21.
- KOSSINNA E. (1921) Die Tiefen des Wiltmeres. *Berlin* **68**, 24.

- KRUMBEIN W. C. (1951) Occurrence and lithologic associations of evaporites in the U.S. *J. Sediment. Petrol.* **21**, 63–81.
- KULP J. L., AULT W. U. and FEELY H. W. (1956a) Sulfur isotope abundances in sulfide minerals. *Econ. Geol.* **51**, 139–149.
- KULP J. L., BATE G. L., AULT W. U. and FEELY H. W. (1956b) Lead and sulfur isotope abundances in the Mississippi Valley galenas. *Bull. Geol. Soc. Amer.* **67**, 123–124.
- MACNAMARA J., FLEMING W., SZABO A. and THODE H. G. (1952) The isotopic constitution of igneous sulphur and the primordial abundance of the terrestrial sulphur isotopes. *Canad. J. Chem.* **30**, 73.
- MACNAMARA J. and THODE H. G. (1950) Comparison of the isotopic constitution of terrestrial and meteoritic sulfur. *Phys. Rev.* **78**, 307–308.
- MACNAMARA J. and THODE H. G. (1951) The distribution of S^{34} in nature and the origin of native sulphur deposits. *Research* **4**, 582.
- McKELVEY V. E., SWANSON R. W. and SHELDON R. P. (1953) *The Permian Phosphate Deposits of Western United States*. Congress Geologique Internatl. Comptes Rendes de la Dix-neuvieme session, Alger 1952, pp. 45–64.
- NOETZLIN J. (1952) La Mesure des Rapports Isotopiques et ses Applications Possibles a la Volcanologie. *Bull. Volcanol.* **12**, 115–125.
- POLDERVAART A. (1955) *Crust of the Earth*. Symposium, Geol. Soc. Amer. Spec. Paper **62**, pp. 119–144.
- RANKAMA K. (1954) *Isotope Geology* pp. 278–286. McGraw-Hill, New York.
- RUBEY W. W. (1951) Geologic history of seawater. *Geol. Soc. Amer. Bull.* **62**, 1111–1148.
- SAKAI H. (1957) Fractionation of sulphur isotopes in nature. *Geochim. et Cosmochim. Acta* **12**, 150–169.
- SENTLE F. E. and BRACKEN J. T. (1955) Theoretical effect of diffusion on isotopic abundance ratios in rocks and associated fluids. *Geochim. et Cosmochim. Acta*, **7**, 61–76.
- SILVERMAN S. R. (1951) The isotope geology of oxygen. *Geochim. et Cosmochim. Acta* **2**, 26–42.
- SLOSS L. L. (1957). Personal communication.
- SVERDRUP H. W., JOHNSON M. W., and FLEMING R. H. (1942) *The Oceans*. Prentice-Hall, New York.
- SZABO A., TUDGE A., MACNAMARA J. and THODE H. G. (1950) The distribution of S^{34} in nature and the sulphur cycle. *Science* **3**, 464–465.
- THODE H. G. (1949) Variations in abundances of isotopes in nature. *Research* **2**, 154–161.
- THODE H. G., KLEEREKOPER H. and McELCHERAN D. (1951) Isotope fractionation in the bacterial reduction of sulphate. *Research* **4**, 581–582.
- THODE H. G. and MACNAMARA J. (1953) The distribution of S^{34} in nature. Mass Spectroscopy in Physics Research, U.S. Dept. of Comm., NBS Circular **522**, 235–241.
- THODE H. G., MACNAMARA J. and COLLINS C. B. (1949) Natural variations in the isotopic content of sulphur and their significance. *Canad. J. Research* **27B**, 361–373.
- THODE H. G., MACNAMARA J. and FLEMING W. H. (1953) Sulphur isotope fractionation in nature and geological and biological time scales. *Geochim. et Cosmochim. Acta* **3**, 235–243.
- THODE H. G., WANLESS R. K. and WALLOUGH R. (1954) The origin of native sulphur deposits from isotope fractionation studies. *Geochim. et Cosmochim. Acta* **5**, 288–298.
- TROFIMOV A. (1949) Isotopic constitution of sulphur in meteorites and in terrestrial objects *Dokl. Akad. Nauk. S.S.S.R.* **66**, 181–184 (Ir Russian); Abstract: *Chem. Abstr.* 43, 6078c.
- VINOGRADOV A. P., CHUPAKHIN M. S., GRINENKO V. A. and TROFIMOV A. V. (1956a) The isotopic composition of sulfur in connection with the growth of pyrites of sedimentary origin. *Geokhim.* **1**, 96–105.
- VINOGRADOV A. P., CHUPAKHIN M. S. and GRINENKO V. A. (1956b) Isotopic ratios S^{32}/S^{34} in sulfides. *Geokhimiya* **4**, 3–9.
- VINOGRADOV A. P., CHUPAKHIN M. S. and GRINENKO V. A. (1957) Some data on the isotopic composition of the sulfur of sulfides. *Geokhim.* **3**, 183–186.

Über den Isotopengehalt des Kohlenstoffs in Süßwasser-Kalkablagerungen

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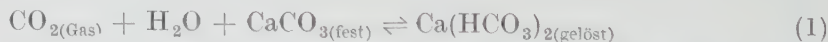
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Abstract—An attempt is made to interpret the observed C^{13}/C^{12} ratio in fresh-water carbonates in terms of the origin of the carbon and the isotope exchange constants involved. Measurements of the isotope ratio of the inorganically dissolved carbon in hard ground waters are reported. It appears that the average depletion in C^{13} content of about 14‰ compared with Solnhofen limestone can be explained quite satisfactorily on this basis. It is shown that the expected isotope ratio of calcium carbonate precipitated from such water is compatible with that of sinter. A few measurements of sinter samples are given and the results on a number of loess samples are discussed. Although considerable caution is necessary when applying isotopic data to geological problems it is felt that with a better understanding of the mechanisms valuable conclusions can be drawn from the C^{13}/C^{12} ratio of carbonates.

BAERTSCHI (1951) und CRAIG (1953) fanden, dass das Kohlenstoffisotopenverhältnis C^{13}/C^{12} in Süßwasser-Kalkablagerungen im allgemeinen kleiner ist als in marinem Kalk.* Beide Autoren ziehen die Möglichkeit in Betracht, dass dies durch Austausch mit Kohlendioxyd organischen Ursprungs verursacht sein könnte, gehen aber auf den möglichen Mechanismus nicht weiter ein. Kürzlich haben CLAYTON und DEGENS (1958) das Kohlenstoff- und Sauerstoffisotopenverhältnis einer Anzahl von Süßwasser- und Meereskalken bestimmt, mit dem Ziel in den Abweichungen des Isotopenverhältnisses ein Kriterium für die Herkunft von Kalksedimenten zu gewinnen. Ihre Messungen bestätigen diejenigen von BAERTSCHI und CRAIG. Als Ursache für die Abweichungen ziehen CLAYTON und DEGENS in Erwägung, dass atmosphärisches Kohlendioxyd von Regenwasser ohne Isotopentrennung aufgenommen und dadurch der Kohlenstoff in der bei der Kalkauflösung entstehenden Kalziumbikarbonatlösung etwas leichter werden könne. Sie stellen weiter die Überlegung an, dass zwischen dem Isotopengehalt von Süßwasserkalk und Landpflanzen ein ähnlicher Unterschied zu erwarten sei wie zwischen Meereskalk und organischer Substanz im Meeré.

Es wird im folgenden gezeigt werden, dass das beobachtete Kohlenstoffisotopenverhältnis von Süßwasserkalk aus den Ablagerungsbedingungen befriedigend erklärt werden kann:

Die Auflösung und Abscheidung von Kalziumkarbonat geschieht nach der Reaktionsgleichung



wobei in der flüssigen Phase in erster Linie Bikarbonationen und gelöstes CO_2 † vorhanden sind. In Meerwasser kommen wegen des hohen Salzgehaltes auch messbare Mengen an Karbonationen vor (WATTENBERG, 1935). In einem solchen

* Das mittlere Konzentrationsverhältnis C^{13}/C^{12} in marinem Kalk ist nach NIER (1950) und CRAIG (1953) etwa 0.01123. Abweichungen des Isotopenverhältnisses einer Kohlenstoffprobe von diesem Standardwert werden mit δ ‰ bezeichnet. Negative Werte für δ bedeuten dabei, dass das C^{13}/C^{12} -Verhältnis beziehungsweise der C^{13} -Gehalt kleiner, der Kohlenstoff also "leichter" ist als in marinem Kalk.

† "Zugehöriges Kohlendioxyd"—WATTENBERG (1935), BÖGLI (1954) und MÜNNICH (1957a,b).

System wird im Gleichgewicht das Isotopenverhältnis des Kohlenstoffs in jeder Komponente bestimmt durch die Gleichgewichtskonstanten der verschiedenen Isotopenaustauschreaktionen. Diese Isotopenaustauschkonstanten sind nicht sehr genau bekannt, die Isotopenverhältnisse in den einzelnen Phasen können jedoch auf Grund von Messdaten des Systems: atmosphärisches Kohlendioxyd—Bikarbonat im Meerwasser—Meereskalk abgeschätzt werden.

Dieses System befindet sich, nach einer allgemeinen Annahme, nahezu im Gleichgewicht. Messungen von CRAIG (1953, 1954) zeigen, dass der anorganisch gelöste Kohlenstoff in Meerwasser im Mittel etwa 2‰ ärmer an C^{13} ist als Meereskalk und etwa 5‰ reicher an C^{13} als atmosphärisches Kohlendioxyd. Diese Relationen sind im linken Teil von Abb. 1 dargestellt. Der Schwankungsbereich der Messungen von CRAIG für die verschiedenen Gruppen ist durch die Höhe der einzelnen Kästchen angedeutet. Unter Zugrundelegung dieser Daten und mit Berücksichtigung der Herkunft des Kohlenstoffs kann das zu erwartende Isotopenverhältnis von Süßwasserkalken abgeschätzt werden.

Auf dem Festland werden Kalksedimente im wesentlichen von hartem Grundwasser abgeschieden. Das im Grundwasser enthaltene Kalziumbikarbonat wird unter der Einwirkung von Kohlendioxyd aus der Humuszersetzung und der Atmung der Pflanzenwurzeln nach Gleichung (1) gebildet. Atmosphärisches Kohlendioxyd spielt dabei, entgegen einer verbreiteten Annahme, keine Rolle. Dies ist in Anbetracht der Tatsache zu verstehen, dass der Kohlendioxydgehalt der Atmosphäre (0,03 Vol %) viel zu klein ist, um die in hartem Grundwasser gefundenen Mengen Kalziumkarbonat in Lösung zu bringen. Um diese aufzulösen, muss der Kohlendioxydpartialdruck um einen Faktor 10–100 grösser sein. Tatsächlich findet man in der Bodenluft in den obersten 10 cm des Bodens im Mittel einen Kohlendioxydgehalt von etwa 0,3 Vol % und in einer Tiefe von 1–2 m sind Kohlendioxydgehalte bis zu 10 und 15 % nicht ungewöhnlich (MEYER und KOEPF, 1958). Auf diese Tatsache wurde bereits von BÖGLI (1954) und MÜNNICH (1957a,b) hingewiesen.

Das Kohlenstoffisotopenverhältnis des im Boden erzeugten Kohlendioxydes ist noch nicht unmittelbar gemessen worden. Es muss jedoch sehr nahe bei dem Isotopenverhältnis von Landpflanzen liegen und zwar aus folgenden Gründen:

(1) Drei sehr stark zersetzte Proben rezenten Holzes zeigen nach Analysen von CRAIG (1954) denselben C^{13} -Gehalt wie normale Landpflanzen.

(2) Der C^{13} -Gehalt von fossilem Holz, von Torf und Kohle liegt nach Analysen verschiedener Autoren (WICKMAN, 1952; CRAIG, 1954) innerhalb des Bereichs normaler Landpflanzen.

(3) Ein Experiment von BAERTSCHI (1953) an Bohnen, die er im Dunkeln keimen liess, zeigte, dass das Isotopenverhältnis des ausgeatmeten Kohlendioxydes mit dem der Keimlinge übereinstimmt, dass bei der Atmung also keine Isotopentrennung aufgetreten ist. Es muss aus Punkt (1) und (2) geschlossen werden, dass auch bei dem Zersetzungsprozess im wesentlichen keine Isotopentrennung auftritt, weil sonst auch die verbleibende Substanz eine gewisse Isotopenverschiebung zeigen sollte. Da Landpflanzen im Mittel eine C^{13} -Abweichung von $\delta = -25‰$ aufweisen (WICKMAN, 1952; CRAIG, 1953) muss also für das im Boden entstehende Kohlendioxyd auch $\delta \approx -25‰$ sein. Wird dieses Kohlendioxyd quantitativ zur

Auflösung von Kalk, der im allgemeinen marinen Ursprungs ist, verwendet, so ergibt sich infolge der Mischung von Kohlenstoff verschiedenen Isotopengehaltes ein Isotopenverhältnis, das zwischen den beiden Ausgangsverhältnissen liegt. Berücksichtigt man quantitativ die Grösse der Anteile des biogenen Kohlendioxydes

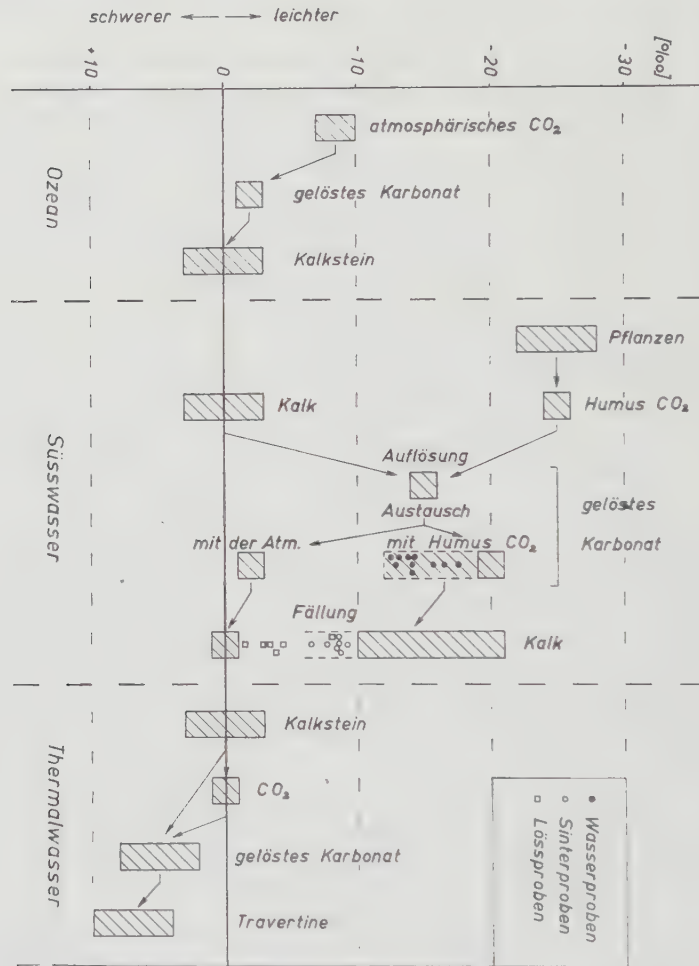


Abb. 1. Isotopengehalt des Kohlenstoffs in natürlichen Systemen. Ordinate: Konzentrationsverhältnis C^{13}/C^{12} , aufgetragen als Promille-Abweichung δ vom Standardwert.

und des Meereskalkes an der entstehenden Kalziumbikarbonatlösung, so erhält man durch die Mischung Kohlenstoff, für den $\delta = -15\text{‰}$ ist (Abb. 1, Mitte). Befindet sich die Lösung im Kontakt mit einer Gasphase, so tritt, da in der flüssigen Phase C^{13} bevorzugt wird, Isotopenaustausch ein, bis die Bikarbonatlösung um etwa 5‰ reicher an C^{13} ist als das Kohlendioxyd in der Gasphase. Ist die Gasphase relativ ausgedehnt, d.h. enthält sie grosse Mengen biogenes Kohlendioxyd, so wird ihr Isotopenverhältnis durch den Austausch praktisch nicht verändert, während der Kohlenstoff in der Bikarbonatlösung (beginnend bei

$\delta = -15\%$) leichter wird, bis er schliesslich eine C^{13} -Abreicherung von $\delta = -20\%$ erreicht hat.

Diese Verhältnisse dürften für die obersten 10 bis 20 cm des Bodens zutreffen, wo die Produktion an Kohlendioxyd sehr hoch ist. In den tieferen Schichten, wo die Kohlenstoffmenge in der Gasphase mit der in der flüssigen Phase vergleichbar wird, geht die Isotopenverschiebung in der Bikarbonatlösung nicht ganz so weit.

Das gelöste Bikarbonat erreicht selbstverständlich nicht das Isotopengleichgewicht mit dem festen Kalk, denn die Diffusion im Festkörper geht so langsam vor sich, dass der Gleichgewichtszustand nur in den alleräussersten Schichten der Kalkteilchen sich einstellen kann.

Die Kalkauflösung muss im wesentlichen innerhalb oder kurz unterhalb der Humusschicht vor sich gehen, denn beim Auflösungs Vorgang werden grosse Mengen gasförmiges Kohlendioxyd verbraucht, so dass es nicht allein auf den Kohlendioxydpartialdruck, sondern auch auf die Menge des verfügbaren Kohlendioxydes ankommt.

Sobald das Wasser mit Hohlräumen in Berührung kommt, die belüftet sind, d.h. einen geringeren Kohlendioxydpartialdruck aufweisen als in der Auflösungszone des Kalks herrscht (Karsthöhlen), oder wenn es als Quelle zu Tage tritt, erfolgt Kalkabscheidung nach Gleichung (1). Geschieht dies langsam, also unter Gleichgewichtsbedingungen, so erfolgt eine C^{13} -Abreicherung von 2% gegenüber dem Kohlenstoff in Lösung. Aus den Experimenten von McCREA (1950) über die Isotopenchemie von Karbonaten ist zu erwarten, dass bei schneller Ausfällung des Kalks das Isotopenverhältnis unverändert bleibt.

Nach diesen Überlegungen sollte der Kohlenstoff in Grundwasser eine C^{13} -Abreicherung gegenüber Meereskalk von etwa 15 bis 20% und der abgeschiedene Süsswasserkalk von etwa 13 bis 20% aufweisen. In eigenen Messungen erhaltene Werte für den Kohlenstoff in Quellwasser und einigen Süsswasser-Kalkablagerungen sind in Tabelle 1 zusammengestellt. Das gelöste Karbonat in den Wasserproben wurde nach dem Verfahren von MUNNICH (1957a) durch Fällung mit Barytlauge quantitativ gewonnen. Der Gehalt der Proben an radioaktivem C^{14} wurde bestimmt und zum Teil bereits veröffentlicht (MÜNNICH, 1957a, b; BRINKMANN, MÜNNICH und VOGEL, 1958).

Die Wasserproben liegen am unteren Rande des erwarteten Bereichs (Abb. 1). Die Isotopenverhältnisse zeigen, dass die Gleichgewichtseinstellung jedenfalls nicht im Kontakt mit einem ausgedehnten Reservoir von gasförmigem biogenen Kohlendioxyd erfolgte. Dies wird bestätigt von den oben erwähnten Messungen des C^{14} -Gehaltes.

Der Kohlenstoff der Sinterproben ist zu schwer, aber immer noch beträchtlich leichter als der im Meereskalk. Dies scheint allgemein so zu sein: Nach den Messungen von BAERTSCHI (1951) und von CLAYTON und DEGENS (1958) ergibt Kalksinter bzw. Süsswasserkalk im Mittel eine C^{13} -Abreicherung von $\delta = -6,7\%$, Messungen von CRAIG (1953) liegen ebenfalls in diesem Bereich. Es besteht die Möglichkeit, dass der Isotopentrennfaktor zwischen Bikarbonat und festem Kalk in Wirklichkeit grösser ist, als er sich aus den Messungen von CRAIG an Meereskalk ergab. Meerwasser enthält ausser Bikarbonat auch beträchtliche Mengen an

Tabelle 1

Probe Nr.*	Beschreibung	C ¹³ -Abweichung δ (‰)†
<i>Wasserproben aus der Umgebung von Heidelberg</i>		
H-154	Grosswasserwerk Mannheim-Rheinau‡	-12,9
H-357	Quelle, Steinbruch Leimen	-13,1
H-152	Pumpwerk Schwimmbad Mosbach‡	-13,8
H-141	Pumpwerk Heidelberg-Handschuhsheim‡	-12,5
H-462-402	Pumpwerk Heidelberg-Handschuhsheim	-14,3
<i>Wasserproben aus dem Braunkohlengebiet bei Köln‡§</i>		
H-480/4-422	Wasserwerk Kenten, Brunnen E 33	-14,1
H-478/2-421	Wasserwerk Wissersheim, Brunnen 80b	-14,1
H-452-393	Wasserwerk Kenten, Brunnen 35	-15,7
H-450-391	Wasserwerk Türnich, Brunnen MT 5	-16,5
H-477/1-420	Zentraltagebau Frechen, Brunnen 96	-17,6
<i>Kalksinterproben</i>		
H-334	Quellkalk, Steinbruch Nussloch b. Heidelberg	-7,7
H-349-316	Poröse Sinterschicht, Doktorshöhle, Muggendorf, Fränk. Jura¶	-6,5
H-348-319	Stalagmit aussen, Doktorshöhle, Muggendorf, Fränk. Jura	-8,6
H-348-320	Stalagmit innen, Doktorshöhle, Muggendorf, Fränk. Jura	-8,6
H-350-327	Sinter, Doktorshöhle, Muggendorf, Fränk. Jura	-8,7
H-412-363	Sinter, Tropfsteinhöhle Wiehl, Oberberg**	-8,5
H-414-417	Sinter, Tropfsteinhöhle Wiehl, Oberberg	-9,2
<i>Lössproben</i>		
H-437-480	Älterer Löss, Baiertal b. Heidelberg	-0,6
H-438-481	Jüngerer Löss, Baiertal b. Heidelberg	-0,8
H-326-335	Löss, Leimen b. Heidelberg	-1,6
H-300-264	Schwemmlöss, 3 m tief, Heidelberg-Neuenheim	-2,9
H-299-262	Schwemmlöss, 1 m tief, Heidelberg-Neuenheim	-3,9
H-298-265	Schwemmlöss, 30 cm tief, Heidelberg-Neuenheim	-3,4
H-297-263	Löss von der Oberfläche, Heidelberg, Philosophenweg	-4,4
H-326-439	Lösskindel, Leimen b. Heidelberg	-8,1

* Probennummern des Heidelberger C¹⁴-Laboratoriums.

† Bezogen auf Solnhofener Kalkstein als Standard.

‡ C¹⁴-Analyse bereits veröffentlicht (MÜNNICH, 1957a,b; BRINKMANN, MÜNNICH und VOGEL, 1958).

Die Proben wurden von den folgenden Herren ausgewählt und zur Verfügung gestellt:

§ Prof. Dr. R. Brinkmann

|| Dr. D. Oswald

¶ Dr. H. W. Franke

** Prof. Dr. M. Schwarzbach

Karbonationen und ist an der Oberfläche überdies noch an Kalziumkarbonat übersättigt (WATTENBERG, 1935). Der Trennfaktor dieser Mischung gegenüber festem Kalk erscheint also kleiner als zwischen reinem Bikarbonat und festem Kalk.*

Liegt also der Isotopengehalt von Kalkabscheidungen im Bereich der "leichten" Karbonate, so ist anzunehmen, dass die Umlagerung unter der Einwirkung von biogenem Kohlendioxyd erfolgte. Allerdings ist dies kein absolutes Kriterium und die geologischen Verhältnisse müssen berücksichtigt werden. So scheinen z.B. Karbonatite im allgemeinen etwas leichter zu sein als Meereskalk, sie haben ein Isotopenverhältnis, welches nahe bei dem von WICKMAN (1956) angenommenen Mittelwert für den Kohlenstoff in der Erdkruste liegt. Dies weist auf den magmatischen Ursprung der Karbonatite hin. Andererseits muss auch Süßwasserkalk nicht unbedingt leichter sein als Meereskalk. Wird Kalk z.B. in einem solchen Süßwassersee abgeschieden, in dem sich das Bikarbonat im Gleichgewicht mit atmosphärischem Kohlendioxyd befindet, so entspricht sein Isotopengehalt dem von Meereskalk.

In dieser Weise erklären sich die Messergebnisse der Lössproben (Tabelle 1). Die Isotopengehalte liegen im selben Bereich wie bei Meereskalk, obwohl im allgemeinen ein erheblicher Teil des in Löss enthaltenen Karbonats unter Einwirkung von Süßwasser umgelagert worden ist. Der hohe C^{13} -Gehalt könnte allerdings dadurch verursacht sein, dass die vorliegenden Lössproben einen überwiegenden Anteil an Trümmern primären Karbonatgesteins enthalten.† Um zu prüfen, inwieweit dies der Fall ist, wurde ein Anschliff der Probe H-437-480 freundlicherweise von I. FORSTER, Mineralogisches Institut, Heidelberg, untersucht. Es zeigte sich, dass von den 30 % $CaCO_3$, die in der Probe enthalten sind, etwa ein Fünftel in Form von primären Karbonatkörnern vorliegt. Der Rest ist sekundäres Kalkbindemittel. Die Tatsache, dass der C^{13} -Gehalt trotzdem so hoch ist, deutet also darauf hin, dass die Bildung des sekundären Kalziumkarbonats, das die Lösskörner umgibt, nicht unter einer dichten Pflanzendecke vor sich ging, sondern sehr wahrscheinlich vor oder kurz nach der äolischen Ablagerung ohne Einwirkung biogener Kohlensäure entstanden ist. Der leichte Kohlenstoff des Lösskindels (H-326-439) dagegen zeigt, dass das Lösskindel später durch Umlagerung des Kalks unter einem bewachsenen Boden entstanden ist. Der relativ leichte Kohlenstoff in den Schwemmlössproben erklärt sich sehr wahrscheinlich ebenfalls aus einer teilweisen späteren Umwandlung, worauf auch der höhere C^{14} -Gehalt hinweist.‡

Neben atmosphärischem und biogenem Kohlendioxyd spielt auch magmatisches Kohlendioxyd eine Rolle bei der Wiederauflösung von Kalkstein. Magmatisches Kohlendioxyd stammt in den meisten Fällen von der thermischen Zersetzung von

* Anmerkung bei der Korrektur: Wie unmittelbare Messungen zeigten, ist dieser Isotopentrennfaktor entgegen der hier geäußerten Vermutung tatsächlich klein. Der einzig wesentliche Trennfaktor in in der ganzen Reihe von gasförmigen Kohlendioxyd bis zum festen Kalk ist der zwischen gelöstem Kohlendioxyd und Bikarbonat. Das gelöste Kohlendioxyd, welches bei der Abscheidung von Kalk aus hartem Wasser entweicht, ist stets beträchtlich C^{13} -ärmer als das vorhandene Bikarbonat. Dadurch reichert sich C^{13} im zurückgebliebenen Bikarbonat an, und auch der C^{13} -Gehalt im abgeschiedenen Karbonat nimmt ständig zu. Das abgeschiedene Karbonat ist im Mittel also um einige Promille reicher an C^{13} .

† Diesen Hinweis verdanke ich Herrn Prof. Dr. C. W. CORRENS.

‡ MÜNNICH und VOGEL, In Vorbereitung.

Kalkstein und hat ein ähnliches Isotopenverhältnis wie dieser. Das gelöste Bikarbonat im Isotopengleichgewicht mit magmatischem Kohlendioxyd wird daher ungefähr 5‰ reicher an C^{13} sein als Kalkstein, durch dessen Zersetzung es gebildet wurde. Darauf folgende Abscheidung kann den Kohlenstoff noch einmal schwerer machen (Abb. 1, rechts). Dies erklärt, warum gewisse Travertine vulkanischen Ursprungs beträchtlich mehr C^{13} enthalten als Meereskalk. Selbstverständlich spielen hier auch Temperatureffekte eine Rolle, wodurch die Isotopentrennfaktoren verschoben werden, so dass definitive Schlüsse erst gezogen werden können, wenn genaue Daten über die Austauschgleichgewichte vorhanden sind.

Es scheint, dass die Kohlenstoffisotopenverhältnisse von Kalkabscheidungen ein brauchbares Hilfsmittel für das Studium der Abscheidungsbedingungen und der Herkunft der Karbonate darstellen. Es ist jedoch wünschenswert, dass genauere Daten über die Austauschgleichgewichte gewonnen werden. Hier sind Experimente im Laboratorium erforderlich, denn die Austauschkonstanten, die aus spektroskopischen Daten, insbesondere soweit sie Bikarbonationen betreffen, errechnet werden können (wie z.B. von STRANKS und HARRIS, 1953), scheinen nicht genügend zuverlässig zu sein.

Für die Auswahl und die Entnahme eines Teiles der Proben sowie für wertvolle Beratung danke ich den Herren Prof. Dr. R. BRINKMANN, Bonn, Dr. H. W. FRANKE, Kreuzpullach b. München, Dr. D. OSWALD, Leimen b. Heidelberg, Prof. Dr. M. SCHWARZBACH, Köln. Den Herren Prof. Dr. L. MEYER und Dr. H. KOEPF sowie Dr. R. N. CLAYTON und Dr. T. DEGENS danke ich für Überlassung ihrer noch unveröffentlichten Manuskripte.

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LITERATUR

- BAERTSCHI P. (1951) *Nature, Lond.* **168**, 288.
 BAERTSCHI P. (1953) *Helv. Chim. Acta* **36**, 1, 773.
 BÖGLI A. (1954) *Die Höhle, Zeitsr. f. Karst- u. Höhlenk.* Wien **5**, 36.
 BRINKMAN R., MÜNNICH K. O. und VOGEL J. C. (1958) *Naturwissenschaften*. Im Druck.
 CLAYTON R. N. and DEGENS T. (1958) Im Druck.
 CRAIG H. (1953) *Geochim. et Cosmochim. Acta* **3**, 53.
 CRAIG H. (1954) *J. Geol.* **62**, 115.
 McCREA J. M. (1950) *J. Chem. Phys.* **18**, 849.
 MEYER L. und KOEPF H. (1958) *Das Kohlendioxyd und die Kohlensäure im Boden, Handbuch d. Pflanzenphysiologie* Bd. V. Springer, Heidelberg. Im Druck.
 MÜNNICH K. O. (1957a) Dissertation Heidelberg.
 MÜNNICH K. O. (1957b) *Naturwissenschaften* **44**, 32.
 NIER A. O. (1950) *Phys. Rev.* **77**, 789.
 STRANKS D. R. and HARRIS G. M. (1953) *J. Amer. Chem. Soc.* **75**, 2012.
 WATTENBERG H. (1935) *Fortsch. Min.* **19**, 168.
 WICKMAN F. E. (1952) *Geochim. et Cosmochim. Acta* **2**, 243.
 WICKMAN F. E. (1956) *Geochim. et Cosmochim. Acta* **9**, 136.

Distribution of certain elements in the Duluth complex

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Abstract—Forty-five samples of mafic rock were obtained at approximately $\frac{1}{2}$ mile intervals along two traverses across the strike of the Duluth complex. From these, spectrographic analyses of olivines, pyroxenes, and plagioclases were made. Along the Ham–Brule traverse, the concentration of elements shows strong local fluctuations but no apparent overall trend. Along the Kawishiwi traverse, the MgO, NiO and Cr₂O₃ of the olivines show a progressive increase upward, whereas the FeO, MnO, CoO, CuO and ZrO₂ decrease upward, and the TiO₂, V₂O₅ and Sc₂O₃ exhibit no consistent trend. Associated feldspars show an upward increase in MnO and CaO; an upward decrease in MgO, FeO, CuO and Na₂O₃; and an erratic variation in NiO and TiO₂.

The trends in the Kawishiwi area are just the reverse of those found in most stratified mafic igneous bodies. They perhaps are the result of multiple injections from a differentiating magma source, with each successive injection emplaced immediately beneath its predecessor. In the Ham–Brule area successive injections were probably cross-cutting, yielding erratic distribution of younger fractions along the traverse line.

INTRODUCTION

THE Duluth complex is a large intrusive body of predominantly mafic igneous rock in north-eastern Minnesota. Its petrology and structure have been described by numerous workers including BAYLEY (1893), GROSH *et al.* (1955), GROUT (1918a,b,c, 1926), NEBEL (1919), SCHWARTZ and DAVIDSON (1952), TAYLOR (1956), WINCHELL and GRANT (1900), and WINCHELL (1900). The complex is crescentic in outcrop pattern, with a length of 160 miles and a maximum width of about 30 miles (Fig. 1). Its average dip is about 15° to the south-east.

This paper describes a study of the elemental distribution in the olivines, pyroxenes and feldspars from gabbroic rocks collected on two traverses across the strike of the complex. One of these, the Ham–Brule traverse, went completely across the mass from the base to the top. The other, or Kawishiwi traverse, sampled somewhat less than the lowermost half, owing to a lack of exposures higher up in the section (Fig. 1). Throughout the paper the term “complex” will be used when referring to the igneous body as a whole. This seems preferable to the term “gabbro complex” as used by TAYLOR (1956) since true gabbro makes up only a fraction of the rock samples studied.

PROCEDURE

Sampling

Along the Ham–Brule traverse, one sample was taken from within each of twenty-eight circles of a $\frac{1}{2}$ mile diameter which are tangent to one another and are aligned perpendicular to the strike of the complex (Fig. 3). Near the top of the mass, two parallel lines of circles about a mile apart were set up, and each successive sample was taken from one or the other. This was necessary owing to the paucity of gabbroic rock in this region, and it is justified if the assumption is made that variation in mineral composition parallel to the strike is negligible

compared to variation across the strike. The Kawishiwi traverse contains seventeen samples which were selected in the same manner except that they do not extend to the top of the complex (Fig. 2). Furthermore, the samples are taken along a line whose basal termination is at the copper-nickel prospect on the Kawishiwi River which is described by SCHWARTZ and DAVIDSON (1952). The

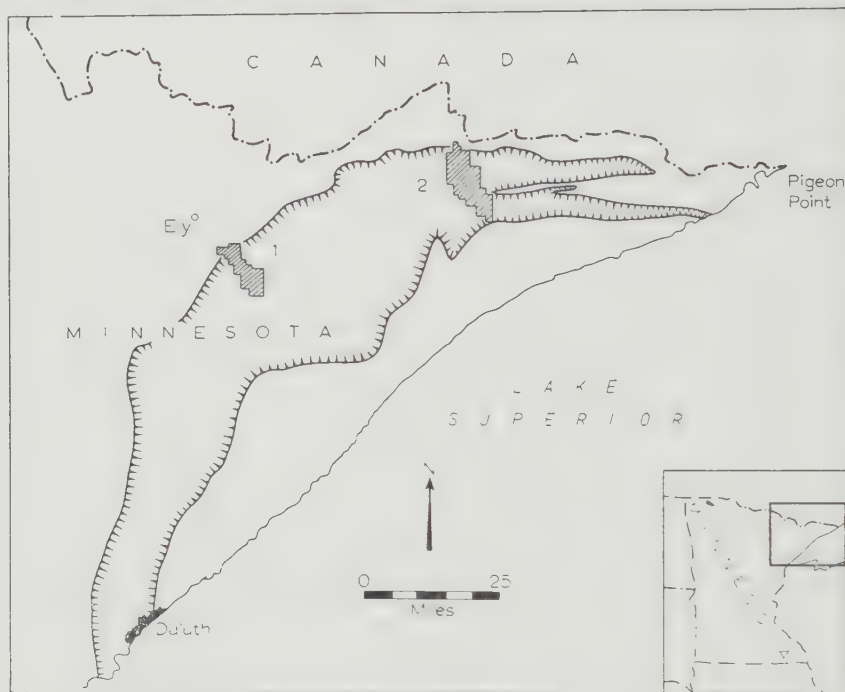


Fig. 1. Index map showing location of Kawishiwi traverse (1) and Ham-Brulé traverse (2) in the Duluth complex. (hashured outline.)

samples in both traverses were numbered consecutively from the base upward, K-1 being at the base of the Kawishiwi traverse and H-1 at the base of the Ham-Brulé traverse.

Crushing and separating

Each of the samples, which averaged between 2-4 in³, was crushed in a steel, hand-operated jaw crusher. This material was then passed through cloth screens, and all between the 80 and 200 mesh sizes was retained. The particle aggregates were separated into their constituent minerals with the aid of a Frantz isodynamic separator and heavy liquids. The separator was used to obtain a concentrate of each of the minerals present (except magnetite which was removed with a hand magnet), and these concentrates were then purified using tetrabromomethane for the plagioclases and Clerici solution for the pyroxenes, olivines and ilmenites.

Optical analyses

Both optical and spectrographic methods were used to determine the Mg/Fe ratio of the olivines. The α - and γ -indices of refraction for the olivine from each

sample were determined using index oils and sodium light. After each determination, the index of the matching oil was checked with a refractometer. An attempt was made to determine the Fe/Mg ratio of the pyroxenes by the same method. The results were not consistent, however, owing to the compound nature of many of

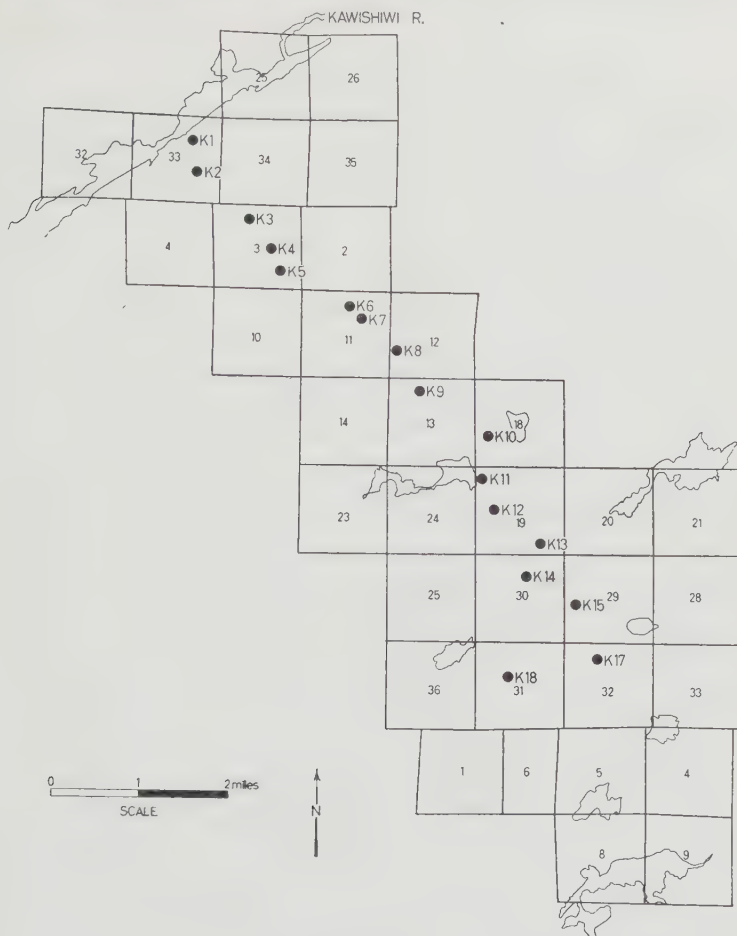


Fig. 2. Sample locations from the Kawishiwi traverse.

the grains. Typically, they consisted of alternating fine plates of orthopyroxene and augite, which had apparently exolved from a mineral of pigeonitic composition. In addition, An content for all the plagioclases was optically determined, using curves from WAHLSTROM (1955, p. 118) for cleavage fragments lying on 001.

Spectrographic analyses

All of the olivines, pyroxenes and plagioclases that could be cleanly separated were analysed spectrographically by O. JOENSUU at the University of Chicago, using a Jarrell-Ash grating spectrograph. The olivines and pyroxenes were analysed for the following: total Fe, MgO, CaO, MnO, NiO, CoO, CuO, ZrO₂, TiO₂, Cr₂O₃, V₂O₃ and Sc₂O₃. The plagioclases were analysed for CaO, K₂O and Na₂O with a



Fig. 3. Sample locations from the Ham-Brule traverse.

flame photometer, and spectrographically for total Fe, MgO, MnO, NiO, CoO, CuO and TiO₂. These data are given in Tables 22-27 at the end of the paper.

In addition to the spectrographic determinations of the individual minerals, chemical analyses of five rocks from the Ham-Brule traverse were made (Table 21).

Accuracy of results

Optical and spectrographic determinations of the fayalite content of the olivines are in good agreement. The largest variation is for sample K-4 in which the olivine was determined as Fa₄₈ optically and Fa_{52.5} spectrographically. In most of the olivines, however, the two methods gave results which were in agreement to within 3 per cent or less.

Correspondence between optically determined and spectrographically determined compositions for the pyroxenes and plagioclases is not so satisfactory. Because of the compound nature of many of the grains of pyroxene, precise optical measurements were very difficult to obtain. Incipient kaolinization of some of the plagioclases has rendered optical determination uncertain, but on the basis of repeated examinations, the maximum error is estimated to be no greater than 5 per cent An.

The accuracy of the spectrographic determinations was influenced in part by the purity of the samples. All the mineral separations contained some impurity in the form of small inclusions. In the olivines these inclusions were very minor and consisted of a very small amount of an opaque mineral, probably ilmenite, in some of the grains. These appear to have had little, if any, effect on the minor element determinations with the possible exception of titanium, for which the measured values may be higher than they should be. The pyroxenes generally contained more inclusions than the olivine, with ilmenite, magnetite, and plagioclase the most common. Some alteration to uralite was also apparent. The analysed plagioclases, some of which are slightly kaolinized, may also have very tiny inclusions of a practically colourless mineral which could be olivine. If so, this would explain their high FeO and MgO values.

The precision of the spectrographic analyses is considered to be within ± 5 per cent of the amount determined for the major constituents, ± 10 per cent for those trace elements that are over 100 p.p.m. and ± 15 per cent for those that are less than 100 p.p.m. (JOENSUU, personal communication). The sodium, calcium and potassium of the feldspars, which were determined by means of flame photometer, have limits of precision as follows: sodium ± 2 per cent; calcium $\pm 5-7$ per cent; and potassium ± 5 per cent.

DISTRIBUTION OF ELEMENTS

In this section, each of the trace elements for which a spectrographic analysis was made is discussed; first with regard to its generally recognized behaviour, and second with reference to its distribution in the olivines, pyroxenes and plagioclases of this study. Tables for each element are included giving the amount of that element in basic rocks and minerals from various areas. Only those rocks are listed that are within the overall compositional range of the Duluth rocks of this study except in cases where data are not available for such rocks. Thus,

from the Skaergaard intrusion only the less iron-rich gabbros are listed, and likewise only the olivines, pyroxenes and plagioclases from these gabbros are given.

Particular emphasis has been placed on the olivines, particularly those of the Kawishiwi traverse. This is because they gave more consistent results than either the pyroxenes or plagioclases, and their analyses are considered more reliable. Olivine from all but one of the Kawishiwi rocks was analysed, whereas many of the Ham-Brule rocks were olivine-free.

Table 1. Radius and electronegativity of a number of ions (from GREEN, 1953)

Ion	Ionic radius	Electronegativity
Al ³⁺	0.51	1.5
Ca ²⁺	0.99	1.0
Co ²⁺	0.72	1.7
Cr ³⁺	0.63	1.6
Cu ⁺	0.96	1.8
Cu ²⁺	0.72	2.0
Fe ²⁺	0.74	1.65
Fe ³⁺	0.64	1.8
K ⁺	1.33	0.8
Mg ²⁺	0.66	1.2
Mn ²⁺	0.80	1.4
Mn ³⁺	0.66	1.5
Na ⁺	0.97	0.9
Ni ²⁺	0.69	1.7
O ²⁻	1.40	3.5
Sc ³⁺	0.81	1.3
Si ⁴⁺	0.42	1.8
Ti ³⁺	0.76	
Ti ⁴⁺	0.68	1.6
V ³⁺	0.74	1.35
V ⁴⁺	0.63	1.6
V ⁵⁺	0.59	1.8
Zr ⁴⁺	0.79	1.4

Iron. In the Duluth complex, iron is a major constituent of the olivines and pyroxenes and is found as a trace element in the feldspars. It has been repeatedly recognized that Fe²⁺ has a slightly greater radius than Mg²⁺ (Table 1). Thus, on the basis of Goldschmidt's rules, Fe²⁺ should be preferentially incorporated in the liquid phase with respect to Mg²⁺. An additional factor to be considered is the electronegativity. RINGWOOD (1955, p. 193) points out that the greater the electronegativity of a cation, the more covalent and less ionic is its bond with oxygen. In a system of crystals forming from a melt, the more ionic a bond is, the greater is its ease of formation and relative stability. Such a bond may be thought of as being "stronger" than one which is more covalent. The more electronegative of a pair of cations will therefore be preferentially incorporated

in the liquid phase, other things being equal. This factor too, would tend to concentrate Fe^{2+} in the later liquid.

The total iron content (recalculated to FeO) of all the olivines analysed spectrographically ranges from 22 to 47 per cent. The distribution is erratic in the olivines from the Ham-Brule traverse (Fig. 4), but in those from the Kawishiwi

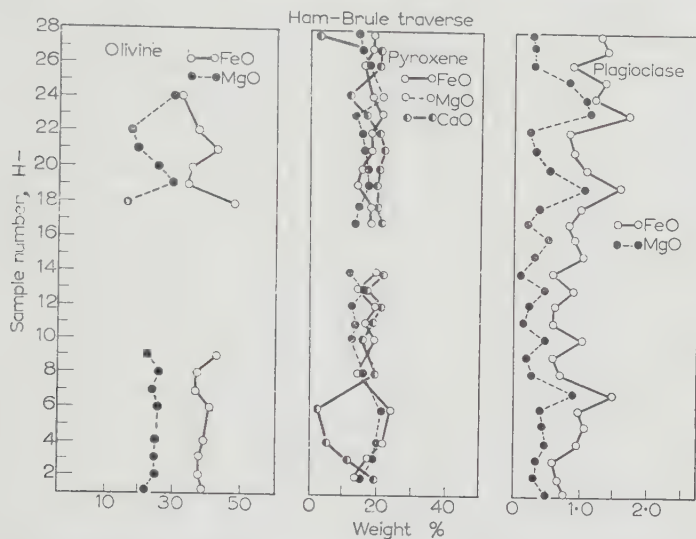


Fig. 4. Distribution of FeO, MgO, and CaO in the olivines, pyroxenes and plagioclases of the Ham-Brule traverse.

traverse, iron exhibits a marked upward decrease (Fig. 5). This trend is accompanied by a corresponding increase in MgO. This is just the reverse of what has been found in such gravity differentiated bodies as the Stillwater complex (HOWLAND *et al.* 1936) and the Skaergaard intrusion (WAGER and DEER, 1939) where the FeO/MgO ratio increases towards the top.

The iron content of the pyroxenes (recalculated to FeO) ranges from 11 to 28 per cent. The upward decrease shown by the Kawishiwi olivines is not so apparent in the pyroxenes, owing to a scarcity of samples.

In the feldspars, iron occurs as a trace element rather than as a major constituent. According to RANKAMA and SAHAMA (1950, p. 659), Fe^{2+} cannot form a feldspar structure. Fe^{3+} may be present, however as a replacement for aluminium. The range in total iron (recalculated to FeO) as determined spectrographically is from nil to 1.3 per cent. There is no apparent trend in the feldspars of the Ham-Brule traverse (Fig. 4), but in the Kawishiwi traverse (Fig. 5) it shows a slight upward increase—a reversal of its behaviour in the associated olivines and pyroxenes. Possibly this is a result of a substitution of Fe^{3+} for aluminium, a greater amount of which is present in the more anorthitic plagioclases near the top of the section (Fig. 6).

Magnesium. In the olivines and pyroxenes of the Duluth complex, MgO varies inversely with the FeO as is to be expected. Thus in the olivines of the Kawishiwi traverse MgO becomes progressively enriched upward until in the top four samples,

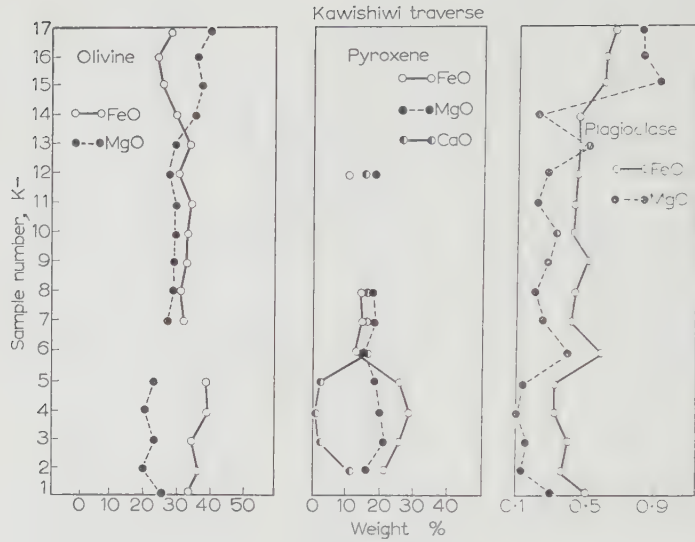


Fig. 5. Distribution of FeO, MgO, and CaO in the olivines, pyroxenes and plagioclases of the Kawishiwi traverse.

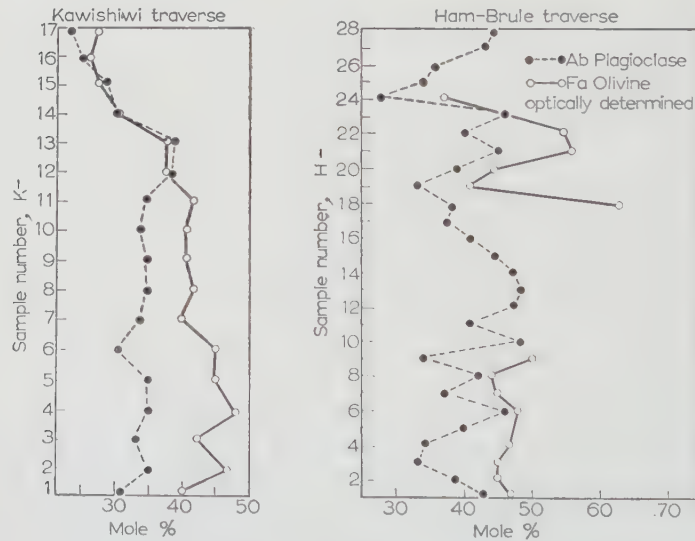


Fig. 6. Composition expressed in terms of albite percentage of the plagioclases and fayalite percentage of the olivines from the Kawishiwi and Ham-Brulé traverses.

the MgO/FeO ratio is greater than 1 (Fig. 5). The total range in MgO in all of the olivines is from 15 to 36 per cent. The distribution curves for MgO in the pyroxenes are difficult to assess owing to the varying amounts of CaO present (i.e. varying orthopyroxene/clinopyroxene ratios). In regions where the CaO content remains relatively constant, however, (samples H-17 through H-21, for example) MgO varies inversely with FeO, and both show fluctuations corresponding with fluctuations of MgO and FeO respectively in the associated olivines (Fig. 4). A rather close correspondence between MgO and FeO in the plagioclases suggests that much of these may be present as inclusions of ferromagnesian minerals.

Calcium. This is present as a trace element in the olivines and as a major constituent of the pyroxenes and feldspars. Its distribution in the last of these is inversely proportional to that of sodium, and the two together may best be represented in terms of albite (Ab) percentage (Fig. 6).^{*} The plagioclases of the Ham-Brule traverse fluctuate erratically. Those from the Kawishiwi traverse are more constant, with the ones from the upper part of the traverse being slightly more anorthitic than those from the base. In the pyroxenes, the amount of calcium present is directly related to the amount of clinopyroxene in the sample. In the olivines, CaO is less than 1 per cent with but two exceptions, and its distribution is erratic in both the Kawishiwi and Ham-Brule traverses (Tables 22 and 25).

Manganese. In silicate minerals, manganese occurs almost exclusively as the divalent ion Mn^{2+} (RANKAMA and SAHAMA, 1950, p. 643). Nearly all of the petrologically important mineral groups contain a manganese-rich variety, but it is not concentrated in most magmas enough to form independent minerals. In the course of crystallization, manganese accompanies iron, and thus increases in the late differentiates. Occasionally Mn^{3+} , like ferric iron, may replace 6-co-ordinated Al^{3+} in silicates, particularly in members of the zoisite-epidote family (GOLDSCHMIDT, 1954, p. 625). GOLDSCHMIDT further states that Mn^{2+} never replaces Ca^{2+} in the feldspars, but WAGER and MITCHELL (1951, p. 193) contradict this by saying: "The fact that the amount in pyroxenes is about the same as in the olivines perhaps suggests that Mn replaces in both Mg/Fe and Ca positions equally easily. The Mn in the feldspars is no doubt replacing Na and Ca."

Table 2 gives the MnO content of a number of mafic rocks. From this it appears that the Duluth rocks are somewhat richer in manganese than comparable rocks from other areas.

Table 3 lists the amount of MnO in the olivines, pyroxenes and plagioclases from four localities. It is always greatest in the olivines, somewhat less in the pyroxenes, and a great deal less in the plagioclases.

The olivines from the Kawishiwi traverse show a noticeable upward decrease in MnO (Fig. 7), which corresponds with a similar decrease in FeO. The MnO/FeO ratio remains quite constant at between 0.013 and 0.018. Consequently, MnO/MgO decreases steadily upward, going from 0.035 to 0.010. RANKAMA and SAHAMA (1950, p. 643) give the MnO/FeO ratio of the average gabbro as 0.017.

^{*} Although these determinations are based on An content, Ab has been plotted (assuming negligible amounts of K_2O) in order to show the corresponding variation of the plagioclases and the olivines, for which Fa is plotted.

Table 2. Percentage MnO in igneous rocks

Aver.	MnO	Rock type	Reference
	Range		
0.15	0.03-0.20	Average gabbro	RANKAMA and SAHAMA (1950)
0.083	0.03-0.20	330 Sudbury norites	STONEHOUSE (1954)
0.14	0.09-0.22	Hawaiian extrusives	WAGER and MITCHELL (1953)
0.132	0.07-0.30	6 Skaergaard gabbros	WAGER and MITCHELL (1951)
0.19	0.12-0.23	5 Ham-Brule traverse gabbros	This study
0.17		2 Basalt chill zones	CORNWALL (1951)
0.12	0.11-0.15	5 Gabbros and norites	NOCKOLDS and MITCHELL (1948)

In the olivines of the Ham-Brule traverse, MnO is relatively constant between 0.48 and 0.60 per cent in the lower part of the traverse, but fluctuates considerably near the top (Fig. 8). There is no apparent trend, although the MnO/FeO ratio varies only slightly, ranging from 0.013 to 0.021.

MnO in the Kawishiwi pyroxenes (Fig. 7), at least over the limited range for which pyroxenes are available from this traverse, decreases upward in general conformity with the MnO in the associated olivines. The correspondence with FeO is good. MnO in the Ham-Brule pyroxenes shows considerable fluctuation, but the MnO/FeO ratio remains relatively constant, confirming the diadochous relationship between manganese and iron in the pyroxene structure.

In the plagioclases from the Kawishiwi traverse, MnO is enriched in the upper four or five samples, but the lower part of the curve is quite uniform at about 0.008 per cent (Fig. 7). Greater fluctuation is shown in the plagioclases from the Ham-Brule traverse (Fig. 8). Despite the decreased amount of MnO, the MnO/FeO ratios remain about the same as they were for the mafic minerals. MnO/FeO ranges from 0.012 to 0.033 in the Kawishiwi plagioclases, and from 0.004 to 0.030 in those from the Ham-Brule traverse. The extremes in this ratio for the Ham-Brule traverse plagioclases are the result of only two or three samples; the normal range is from 0.012 to 0.018. Hence, it appears that in the feldspars as well as the olivines and pyroxenes, the manganese is diadochous with ferrous iron.

The behaviour of MnO in these minerals can be summarized as follows: It is about twenty times as concentrated in the olivines as in the feldspars, but the

Table 3. Percentage MnO in minerals

Location	Olivine		Pyroxene		Plagioclase	
	Average	Range	Average	Range	Average	Range
Ham-Brule	0.60	0.43-1.00	0.40	0.35-0.55	0.014	0.005-0.025
Kawishiwi	0.44	0.32-0.70	0.42	0.25-0.60	0.011	0.005-0.025
Skaergaard*	0.54	0.22-1.00	0.37	0.10-0.77	0.013	0.006-0.026
Greenstone†	0.66	0.52-0.81	0.49	0.32-0.81	0.014	0.006-0.032

* Recalculated to MnO from columns A, B, and C (less iron-rich gabbros), Table B, WAGER and MITCHELL (1951).

† Recalculated to MnO from CORNWALL and ROSE (1957) p. 215.

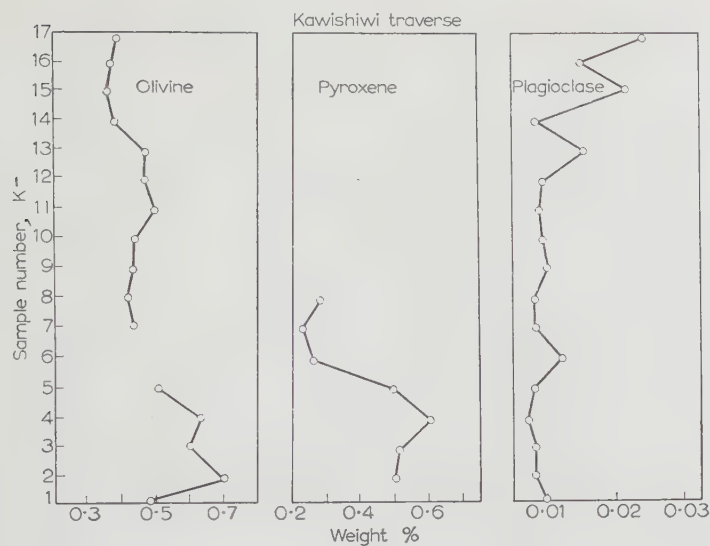


Fig. 7. Distribution of MnO in the olivines, pyroxenes and plagioclases of the Kawishiwi traverse.

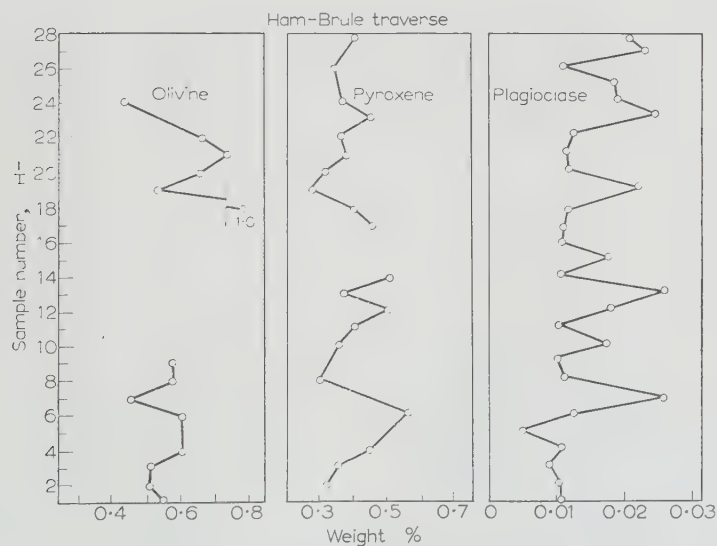


Fig. 8. Distribution of MnO in the olivines, pyroxenes, and plagioclases of the Ham-Brule traverse.

ratio MnO/FeO remains essentially constant throughout the different mineral groups and in the rocks as a whole. The fact that Mn^{2+} is much more closely associated with Fe^{2+} than with either Mg^{2+} or Ca^{2+} is understandable in the light of ionic radius and electronegativity considerations. On the basis of its smaller ionic radius alone, Fe^{2+} would be expected to be incorporated at the expense of Mn^{2+} , but this is compensated for by the higher electronegativity of Fe^{2+} which gives it a more covalent and hence "weaker" bond with oxygen. Both radius and electronegativity favour Mg^{2+} over Mn^{2+} , and that is why the Mn/Mg ratio increases in the later minerals. The difference in radius between Mn^{2+} and Ca^{2+} is so great that they do not readily substitute for one another.

Nickel. Nickel may occur in four different ways in igneous rocks: in silicates, in sulphides, in oxides, and occasionally in iron-nickel alloys. VOGT (1923) concluded that although such rocks contain some nickel in sulphides, the great bulk of it is present in the ferromagnesian silicates. It is most abundant in olivine, and is found in decreasing amounts in orthopyroxene, clinopyroxene, amphibole and biotite. VOGT found a close relationship between nickel and magnesium and concluded that Ni^{2+} substituted for Mg^{2+} in mineral structures, a view since widely accepted. Recently, however, RINGWOOD (1955, p. 197) has suggested that it is much more likely that Ni^{2+} enters the crystal at the expense of Fe^{2+} rather than Mg^{2+} . He points out that on the basis of ionic radii and electronegativities, the $\text{Ni}-\text{O}$ bond should be weaker than that of $\text{Mg}-\text{O}$. On the other hand, Ni^{2+} should form a stronger bond with oxygen than Fe^{2+} , because of its smaller radius and almost equal electronegativity. These deductions are, however, contrary to GOLDSCHMIDT's statement that because of its more homopolar (covalent) character, the $\text{Ni}-\text{O}$ bond is stronger than the $\text{Mg}-\text{O}$ bond (GOLDSCHMIDT, 1944).

Table 4 shows that the five samples of Duluth gabbro average higher in nickel than comparable rocks from other areas; the high value of 700 p.p.m. may be in

Table 4. Nickel in igneous rocks (p.p.m.)

Nickel		Rock type	Reference
Aver.	Range		
160		Average gabbro	GOLDSCHMIDT (1937)*
45		Gabbro and diabase	SAHAMA (1945)*
65		Basic rocks, Sweden	LUNDEGÅRDH (1946)*
110	11-390	59 Ontario diabases	FAIRBAIRN <i>et al.</i> (1953)
179	25-400	6 Skaergaard gabbros	WAGER and MITCHELL (1951)
83	70-100	2 Hawaiian basalts	WAGER and MITCHELL (1953)
210	60-300	6 Gabbros and norites	NOCKOLDS and MITCHELL (1948)
63	17-260	10 Gabbros	WELLS (1943)
440	300-700	5 Ham-Brule traverse gabbros	This study
240		Sudbury lopolith	STONEHOUSE (1954)
97	20-110	17 Subsilicic rocks	SANDELL and GOLDICH (1943)
166	50-460	19 Keweenawan basalts	CORNWALL and ROSE (1957) p. 213
124	30-300	5 Ontario norites	FRIEDMAN (1957) p. 1560
63	8-152	21 Lambertville diabases	STORM and HOLLAND (1957)

* From FAIRBAIRN *et al.* (1953) p. 45.

Table 5. NiO in minerals (p.p.m.)

Location	Olivine		Pyroxene		Plagioclase	
	Aver.	Range	Aver.	Range	Aver.	Range
Ham-Brule	805	270-1300	189	12-400	15	nil-70
Kawishiwi	1335	700-2900	422	220-670	10	3-25
Skaergaard*	1162	325-2000	130	50-200	3	nil-10
Greenstone†	1410	820-2000	165	2-380	25	7-100
Lambertville‡			116	10-305	13	

* Recalculated to NiO from columns A, B, and C (less iron-rich gabbros), Table B, WAGER and MITCHELL (1951).

† Recalculated to NiO from CORNWALL and ROSE (1957) p. 215.

‡ Recalculated to NiO from STORM and HOLLAND (1957) p. 340.

error. If it is discarded, the remaining samples are in general agreement with the higher nickel rocks from elsewhere.

Table 5 shows that the average nickel content from the Duluth olivines is approximately 1000 p.p.m., which is in accord with its concentration in olivines from other areas. In the Ham-Brule traverse, NiO shows wide local fluctuations without any apparent trend (Fig. 9). In the Kawishiwi traverse olivines (Fig. 10), NiO remains constant at just over 1000 p.p.m. except for the upper three samples which show a marked increase to well over 2000 p.p.m. This jump is reflected in the NiO/FeO ratio which otherwise remains relatively constant at from 0.0025 to 0.0040. NiO/MgO, although erratic, generally increases with increasing MgO in accordance with the findings of SANDELL and GOLDICH (1943, p. 117), who have stated that although the distribution coefficient K^* for Ni and MgO is always greater than one, it decreases with decreasing MgO.

The NiO of the pyroxenes from the Kawishiwi traverse (Fig. 10) reaches a maximum near the base and then decreases upward. The NiO curve, however, is essentially the reverse of the CaO curve (Fig. 5), suggesting that nickel is incorporated preferentially in orthopyroxene with respect to clinopyroxene.

In plagioclases of the Kawishiwi traverse the NiO distribution curve is very similar to that for the associated olivines (Fig. 10). NiO in the Ham-Brule plagioclases (Fig. 9) remains essentially constant at between 5 and 30 p.p.m., except for a few samples which are higher, probably as a result of impurities.

No definite relationship between nickel and either magnesium or iron can be established on the basis of these data. In general, however, the increase of NiO in the upper olivines from the Kawishiwi traverse suggests that Ni proxies more readily for Mg than for Fe. RINGWOOD's suggestion that because of similar ionic radii and electronegativities, nickel-iron diadochy is of primary importance, does not explain why, when Fe^{2+} , Mg^{2+} , and Ni^{2+} are in competition for a given structural position, Ni^{2+} is preferentially incorporated with respect to Mg^{2+} as stated by SANDELL and GOLDICH (1943, p. 117), and as was found to a limited extent in the Kawishiwi olivines. On these bases, Ni^{2+} should be enriched with

$$* \quad \frac{\text{Ni (solid)}}{\text{MgO (solid)}} = K \frac{\text{Ni (liquid)}}{\text{MgO (liquid)}}$$

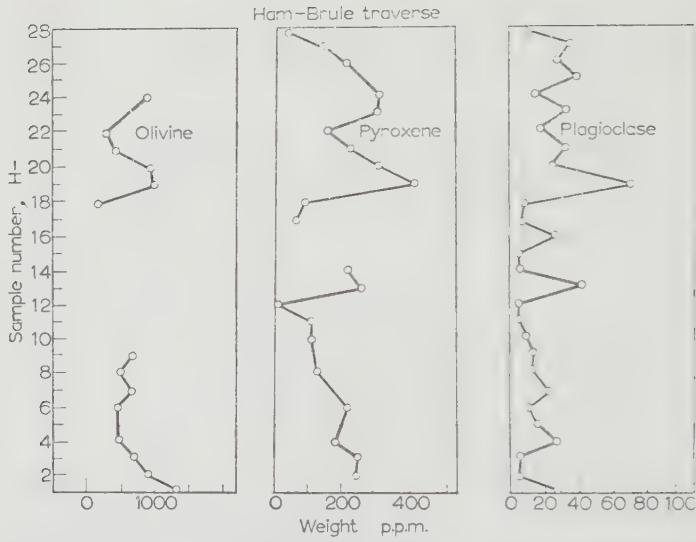


Fig. 9. Distribution of NiO in the olivines, pyroxenes and plagioclases of the Ham-Brule traverse.

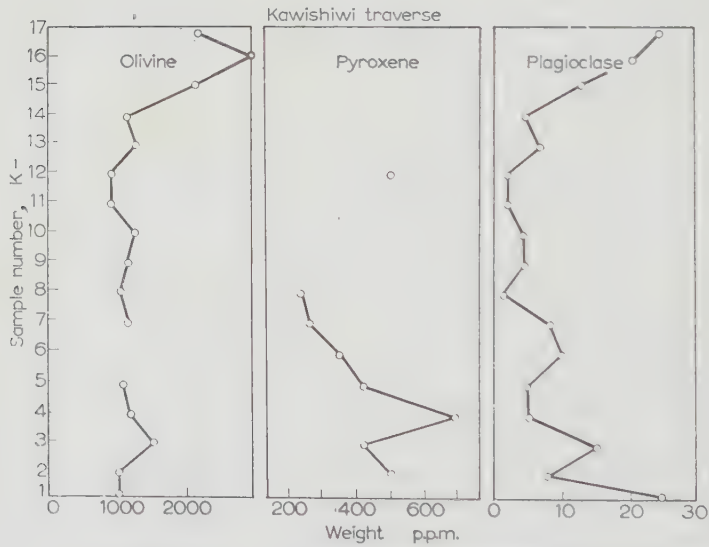


Fig. 10. Distribution of NiO in the olivines, pyroxenes, and plagioclases of the Kawishiwi traverse.

Table 6. Cobalt in mafic igneous rocks (p.p.m.)

Cobalt		Cobalt Rock type	Reference
Aver.	Range		
79		Average gabbro	RANKAMA and SAHAMA (1950)
54	30-80	6 Gabbros	WAGER and MITCHELL (1951)
40	10-74	59 Diabases	FAIRBAIRN <i>et al.</i> (1953)
37	19-55	3 Duluth gabbros	FAIRBAIRN <i>et al.</i> (1953)
33	30-40	3 Hawaiian basalts	WAGER and MITCHELL (1953)
63	30-100	6 Gabbros, & norites	NOCKOLDS and MITCHELL (1948)
32	28-55	16 Subsiliic rocks	SANDELL and GOLDICH (1943)
41	33-53	19 Keweenawan basalts	CORNWALL and ROSE (1957) p. 213
44	20-70	5 Ontario norites	FRIEDMAN (1957) p. 1560

respect to Fe^{2+} , but depleted with respect to Mg^{2+} , and hence show a differentiation trend intermediate between the two. It may be that some as yet unconsidered factors play a part. Such a possible factor is the formation of oxygen-nickel complexes in a melt, which would tend to cause the nickel to concentrate in the late stages (RINGWOOD, 1955, p. 249). Most crystallizing melts may contain nickel both as Ni^{2+} and as nickel-oxygen complexes.

Cobalt. The distribution of cobalt in igneous rocks is very similar to that of nickel, and the two are commonly associated. In silicates, it occurs as Co^{2+} , and has been thought to be camouflaged by Fe^{2+} (GOLDSCHMIDT, 1954, p. 667). SANDELL and GOLDICH (1943, p. 178), however, found the Co/Mg ratio to be much more consistent over a wide range than the Co/Fe ratio. Nickel is enriched with respect to cobalt in the early silicate phases by more than 10 to 1, but this ratio decreases with differentiation until in the silicic rocks, cobalt may actually be more abundant, although both will be very low (RANKAMA and SAHAMA, 1950, p. 680). LUNDEGÅRDH (1946, p. 150) has suggested that the Ni/Co ratio can be used to estimate the stage of differentiation and this has been confirmed by WAGER and MITCHELL (1951, p. 189) for the basic and intermediate rocks.

Table 6 gives average cobalt concentrations in gabbros and basic rocks from a number of different areas. No cobalt analyses are available for the rocks from this study, but CoO in the olivines, pyroxenes, and plagioclases from the Ham-Brule and Kawishiwi traverses is given in Table 7. These minerals seem to be slightly higher in CoO than those from the Skaergaard intrusion. The high value of 500 p.p.m. in the Ham-Brule olivines is somewhat anomalous, however, and may well be due to sulphide contamination.

Table 7. CoO in minerals (p.p.m.)

Location	Olivine		Pyroxene		Plagioclase	
	Aver.	Range	Aver.	Range	Aver.	Range
Ham-Brule	315	230-500	88	50-130	2	0-12
Kawishiwi	352	270-420	148	100-210	not detectable	
Skaergaard*	174	159-191	67	63-76	trace	
Greenstone†	292	292-292	104	63-122	24	0-127

* Recalculated to CoO from columns A, B, and C (less iron-rich gabbros), Table B, WAGER and MITCHELL (1951).

† Recalculated to CoO from CORNWALL and ROSE (1957) p. 215.

CoO in the Kawishiwi olivines shows a slight upward decrease (Fig. 11), and in the Ham-Brule traverse it is erratic with no recognizable trend (Fig. 12). The CoO/MgO and CoO/FeO ratios for the Kawishiwi olivines were plotted (Fig. 11). CoO/MgO decreases steadily upward whereas CoO/FeO remains constant overall but shows greater fluctuations. In the pyroxenes CoO, like NiO, fluctuates reciprocally with CaO, indicating that cobalt is concentrated in the orthopyroxenes.

Table 8. Copper in mafic igneous rocks (p.p.m.)

Aver.	Copper		Rock type	Reference
		Range		
126		20-162	25 Subsiliic rocks	SANDELL and GOLDBICH (1943)
69		12-120	59 Ontario diabases	FAIRBAIRN <i>et al.</i> (1953)
37		19-55	3 Duluth gabbros	FAIRBAIRN <i>et al.</i> (1953)
440		280-600	2 Basalt chill zones	CORNWALL (1951)
133		100-200	3 Hawaiian basalts	WAGER and MITCHELL (1953)
92		50-200	6 Skaergaard gabbros	WAGER and MITCHELL (1951)
114		51-200	19 Keweenawan basalts	CORNWALL and ROSE (1957) p. 213
38		10-80	5 Ontario norites	FRIEDMAN (1957) p. 1560

CoO could be detected in about half of the Ham-Brule feldspars, but it was not found at all in those from the Kawishiwi traverse. In those feldspars where it was found, it generally corresponded to peaks in the MgO, FeO, and NiO curves (Fig. 12) and was probably present in inclusions of mafic minerals.

Considerations of ionic radius and electronegativity suggest that Co^{2+} should proxy for Fe^{2+} in silicate minerals, and that it should be enriched with respect to Mg^{2+} in the later differentiates. This appears to be the situation in the Kawishiwi traverse olivines, assuming the differentiation trend to be from the top downward as is indicated by the distribution of FeO, MgO, etc. In the Kawishiwi pyroxenes also, the CoO curve matches the FeO curve slightly better than that of MgO. Thus, these results correspond with those of GROSH *et al.* (1955, p. 17) who found cobalt to increase steadily with increasing iron content in olivines from the sulphide-rich area along the Kawishiwi River.

Copper. Copper is commonly found in the sulphide phase, although it may be present as a trace in some silicates. When this happens, it is thought to be present as Cu^+ where it is camouflaged by Na^+ , or as Cu^{2+} where it probably replaces Fe^{2+} (RINGWOOD, 1955, p. 195).

Table 8 gives the copper content of a number of basic rocks. The six gabbros from the Skaergaard intrusion were similar in iron content to the ones studied from the Duluth complex. However, some of the more iron-rich rocks from the Skaergaard intrusion contain up to 700 p.p.m. copper.

As with CoO, the CuO in the minerals from the two Duluth traverses (Table 9) appears to be higher than in the corresponding minerals from the other areas. This is particularly noticeable in the olivines and at first suggests that some copper sulphide contamination was present in the sample. If this were true, however, an erratic or random distribution would be expected. Instead, the CuO

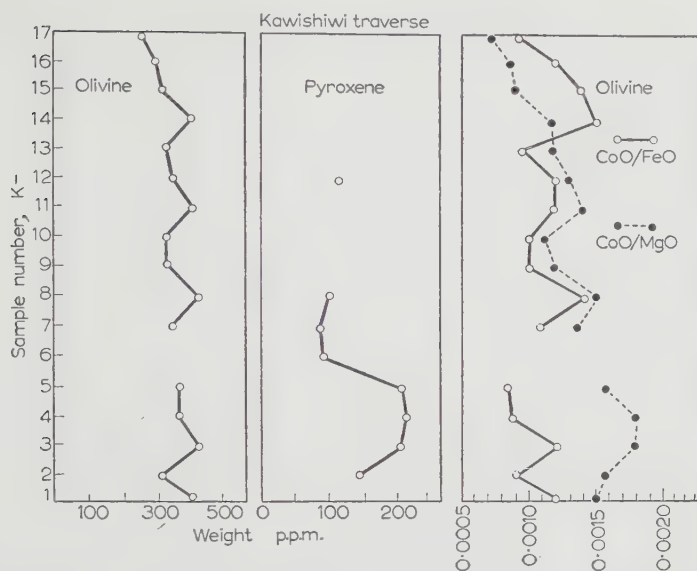


Fig. 11. Distribution of CoO in the olivines and pyroxenes and CoO/MgO and CoO/FeO ratios in the olivines, Kawishiwi traverse.

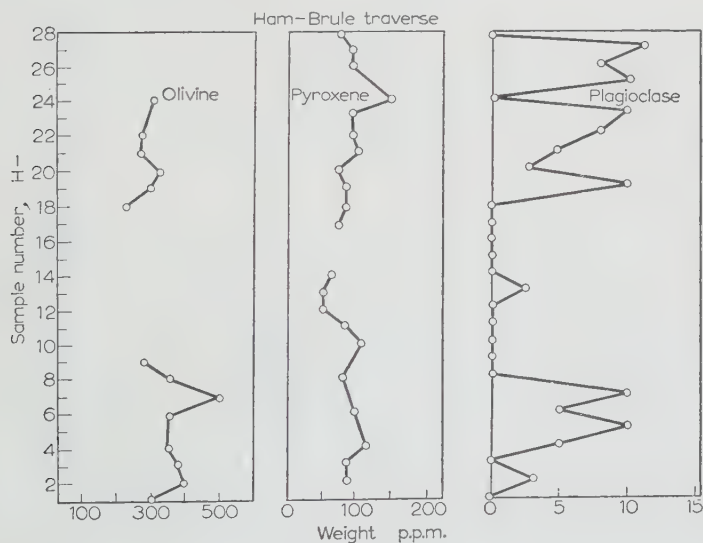


Fig. 12. Distribution of CoO in the olivines, pyroxenes and plagioclases of the Ham-Brule traverse.

Table 9. CuO in minerals (p.p.m.)

Location	Olivine		Pyroxene		Plagioclase	
	Aver.	Range	Aver.	Range	Aver.	Range
Ham-Brule	219	40-1200	290	55-900	80	10-220
Kawishiwi	212	10-700	227	60-550	36	15-80
Skaergaard*	25	25-25	54	0-125	28	19-44
Greenstone†	46	44-48	160	48-400	45	25-88

* Recalculated to CuO from columns A, B, and C (less iron-rich gabbros), Table B, WAGER and MITCHELL (1951).

† Recalculated to CuO from CORNWALL and ROSE (1957) p. 215.

in the Kawishiwi olivines shows a marked decrease upward (Fig. 13), indicating that in this mineral Cu^{2+} probably proxies for Fe^{2+} . This comparison between the copper contents of the Duluth and Skaergaard minerals is slightly misleading, as in the more iron-rich rocks of the Skaergaard, Cu^{2+} is present up to 700 p.p.m. in the olivines, and up to 1000 p.p.m. in the pyroxenes.

In the minerals from the Ham-Brule traverse, no trends show up in the CuO distribution (Fig. 14), and the lack of correspondence between high values for associated minerals suggests that these may be influenced by sulphide contamination.

There does seem to be a very general relationship between CuO and FeO in the olivines and pyroxenes, and between CuO and Na_2O in the feldspars. In the Kawishiwi olivines, CuO and FeO are both enriched near the base, although CuO is enriched to a somewhat greater extent. In the Kawishiwi feldspars, CuO shows a correspondence with percentage albite, but its trend is just the opposite to that of total iron (calculated as FeO) which occurs as a trace. Thus copper in the feldspars is probably present as Cu^+ replacing sodium. Similar relationships can be seen in the Ham-Brule traverse.

RINGWOOD (1955, p. 196) has pointed out that on the basis of their respective ionic radii and electronegativities, Cu^{2+} should proxy most readily for Fe^{2+} in a melt. These two factors indicate that the Cu-O bond should actually form a little less readily than the Fe-O bond, so that the late stages should be considerably enriched in copper. A similar argument holds for the relationship between Cu^+ and Na^+ in the feldspars. Thus copper tends to build up in a magma until it is sufficiently concentrated to form an immiscible sulphide phase. This is apparently the situation in the Skaergaard intrusion (WAGER and MITCHELL, 1951, p. 190) and also shows up at one place in the Duluth complex, where the copper prospect on the Kawishiwi River may be considered to terminate the progressive northward increase of copper in the Kawishiwi olivines.

Titanium. Titanium averages 0.44 per cent in igneous rocks which is roughly one-fifth the content of magnesium (RANKAMA and SAHAMA, 1950, p. 557). Most of it occurs as Ti^{4+} in independent titanium minerals such as ilmenite, FeTiO_3 ; rutile, TiO_2 ; and sphene, $(\text{CaTi}(\text{O},\text{OH},\text{F})(\text{SiO}_4))$, of which ilmenite is the most common. Titanium is found in greatest abundance in gabbroic rocks and appears to reach a maximum at an early, but not the earliest, stage of crystallization.

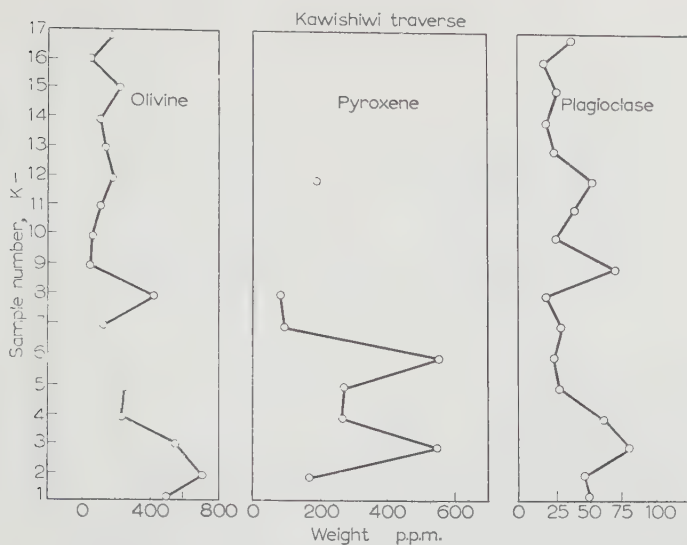


Fig. 13. Distribution of CuO in the olivines, pyroxenes and plagioclases of the Kawishiwi traverse.

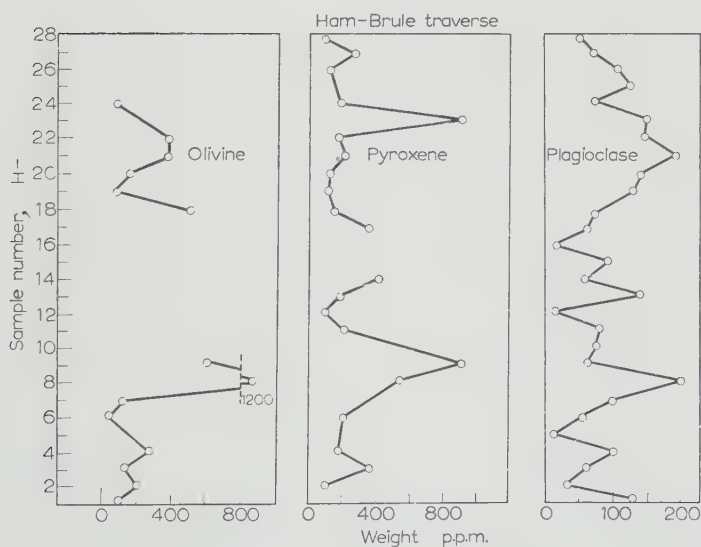


Fig. 14. Distribution of CuO in the olivines, pyroxenes and plagioclases of the Ham-Brule traverse.

Table 10. Percentage of TiO_2 in mafic igneous rocks

TiO_2 range	Rock type	Reference
1.98-4.43	3 Hawaiian basalts	WAGER and MITCHELL (1953)
0.55-2.64	6 Skaergaard gabbros	WAGER and MITCHELL (1951)
0.88-3.60	5 Ham-Brule trav. gabbros	This study
0.15-0.34	6 Bushveld norites	DALY (1928) p. 727
1.13	26 Norites, average	DALY (1928) p. 727
2.02	Chill zone, Greenstone flow	CORNWALL (1951)
0.20-0.45	4 Norites, Ontario	FRIEDMAN (1957) p. 1559

Table 10 gives the TiO_2 content of a number of typical basic rocks. TiO_2 content of the gabbros from the Ham-Brule traverse is similar to that of the Skaergaard gabbros and Hawaiian basalts.

RANKAMA and SAHAMA (1950, p. 561) give 0.7 per cent TiO_2 as the maximum that may be present in augite. The Duluth gabbro pyroxenes, which average 0.8 per cent TiO_2 (Table 11), are thus somewhat high, which may possibly be a result of the schiller structure in many of them. These pyroxene values are not excessive, however, when compared with TiO_2 in the pyroxenes from the Skaergaard intrusion and Greenstone flow.

Titanium shows no noticeable trends in any of the analysed mineral groups except for the Kawishiwi traverse feldspars where it is surprisingly regular in amount (Fig. 15). Its distribution curve in the pyroxenes is characterized by local highs and lows which bear no apparent relationship to those of any other mineral (Figs. 15 and 16).

Ti^{4+} ordinarily does not replace Si^{4+} in silicate minerals because of the large difference in ionic radius (GOLDSCHMIDT, 1954, p. 411). On the basis of radius and electronegativity (Table 1), Ti^{4+} would be expected to substitute most readily for Fe^{3+} . MASON (1952, p. 117) suggests that in pyroxene, hornblende and biotite, Ti^{4+} proxies for Al^{3+} in six-fold co-ordination. If the titanium is present as Ti^{3+} , it would most likely proxy for Fe^{3+} . In the presence of iron, however, Ti^{4+} cannot be analytically distinguished from Ti^{3+} .

Table 11. Percentage of TiO_2 in minerals

Location	Olivine		Pyroxene		Plagioclase	
	Aver.	Range	Aver.	Range	Aver.	Range
Ham-Brule	0.40	0.04-1.3	0.84	0.34-1.35	0.093	0.045-0.22
Kawishiwi	0.40	0.05-1.2	0.75	0.3-1.5	0.128	0.07-0.13
Skaergaard*		trace	1.17	0.87-1.71		
Greenstone†	0.27	0.20-0.33	1.00	0.22-2.00	0.060	0.05-0.062

* Recalculated to TiO_2 from columns A, B, and C, (less iron-rich gabbros), Table B, WAGER and MITCHELL (1951).

† Recalculated to TiO_2 from CORNWALL and ROSE (1957) p. 215.

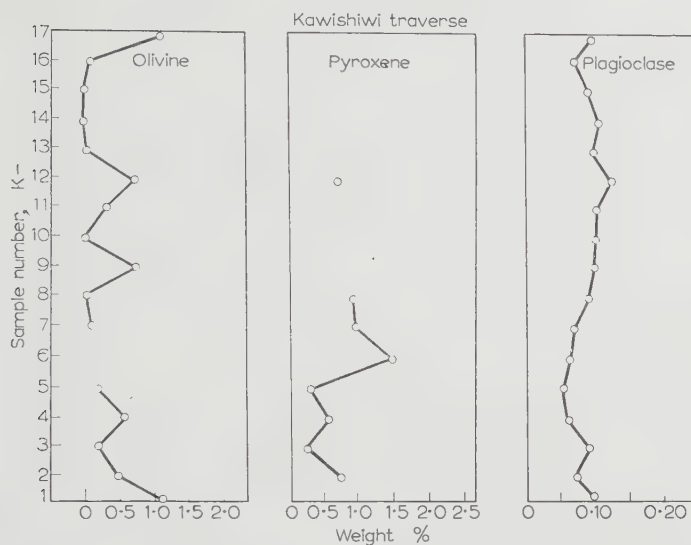


Fig. 15. Distribution of TiO_2 in the olivines, pyroxenes and plagioclases of the Kawishiwi traverse.

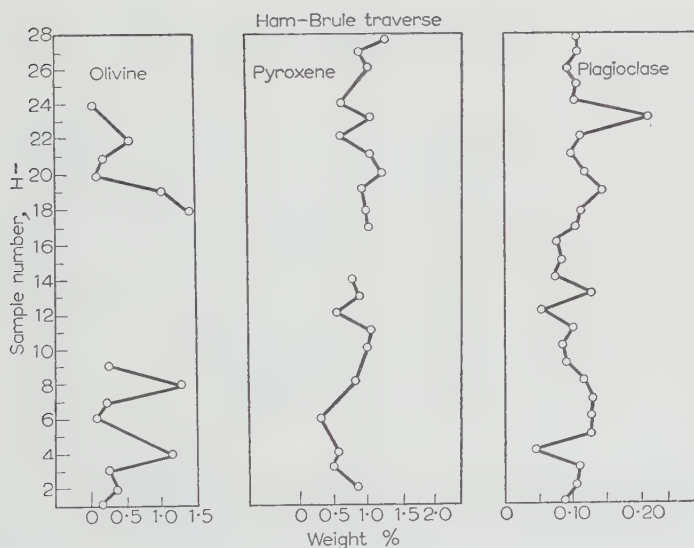


Fig. 16. Distribution of TiO_2 in the olivines, pyroxenes and plagioclases of the Ham-Brue traverse.

Table 12. Zirconium in mafic igneous rocks (p.p.m.)

Zirconium range	Rock type	Reference
50-150	6 Skaergaard gabbros	WAGER and MITCHELL (1951)
50-150	3 Hawaiian basalts	WAGER and MITCHELL (1953)
13-260	59 Ontario diabases	FAIRBAIRN <i>et al.</i> (1953)
140	Gabbros	FAIRBAIRN <i>et al.</i> (1953)
		RANKAMA and SAHAMA (1950)
260-360	3 Duluth gabbros	FAIRBAIRN <i>et al.</i> (1953)
30-100	6 Gabbros and norites	NOCKOLDS and MITCHELL (1948)
10-1500	202 Igneous rocks, SiO ₂ 45-55%	POLDERVAART (1956)
50-200	19 Keweenawan basalts	CORNWALL and ROSE (1957) p. 213

Zirconium. Zirconium is thought to be present in silicates exclusively as Zr⁴⁺, and the bulk of it is concentrated in the mineral zircon according to most workers. It is, however, found as a trace in such minerals as olivine, pyroxene and apatite (WAGER and MITCHELL, 1951, p. 192), and POLDERVAART, (1956, p. 524) suggests that "in the more mafic basaltic rocks . . . most of the zirconium occurs in the pyroxene lattice, and not as zircon".

Table 12 gives the zirconium content of a number of basic rocks. These values may be compared with the very late liquid of the Skaergaard intrusion (after the magma is 95 per cent solidified) which has as much as 800 p.p.m. Zr⁴⁺ (WAGER and MITCHELL, 1951, Table B), or the more siliceous differentiates of the Hawaiian lavas (oligoclase andesites and soda trachytes) which contain up to 1500 p.p.m (WAGER and MITCHELL, 1953, p. 218).

Table 13 shows that zirconium is higher in pyroxenes than in olivines, and that the Duluth pyroxenes fall between those of the Skaergaard intrusion and the Greenstone flow in their zirconium content. The Kawishiwi traverse olivines, however, contain ZrO₂ in amounts of up to 380 p.p.m. (Fig. 17), and the distribution curve is very similar to that of MnO for the same group of olivines. In the pyroxenes of the Ham-Brule traverse, the ZrO₂ and MnO curves show a similar, although not so well defined, relationship, but the curves are quite dissimilar in the pyroxenes from the Kawishiwi traverse.

Table 13. ZrO₂ in minerals (p.p.m.)

Location	Olivine		Pyroxene	
	Aver.	Range	Aver.	Range
Ham-Brule		(all < 100)	165	100-400
Kawishiwi	144	80-380	226	150-330
Skaergaard*		trace	43	35-59
Greenstone†		none	400	0-2400
Europe-Diverse‡	48	47-51	92	14-156

* Recalculated to ZrO₂ from columns A, B, and C (less iron-rich gabbros), Table B, WAGER and MITCHELL (1951).

† Recalculated to ZrO₂ from CORNWALL and ROSE (1957) p. 215.

‡ Recalculated to ZrO₂ from DEGENHARDT (1957) p. 282.

A close similarity in distribution would be expected between Zr^{4+} and Mn^{2+} on the basis of their radii and electronegativities. But, in order for Zr^{4+} to assume the role of Mn^{2+} in a crystal structure, there must be a compensation for the excess charge. Possibly Al^{3+} substitutes for Si^{4+} in the tetrahedral position. Although such a substitution does not take place to any great extent in

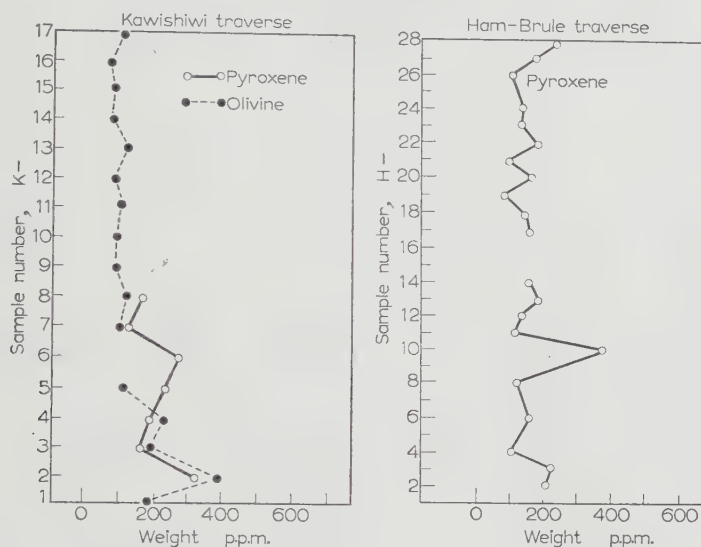


Fig. 17. Distribution of ZrO_2 in the pyroxenes and olivines of the Kawishiwi traverse, and in the pyroxenes of the Ham-Brule traverse.

orthosilicates (RAMBERG, 1952, p. 344), there is on the average, from 3000 to 4000 p.p.m. Al_2O_3 in the Kawishiwi olivines, and the resulting charge deficiency may be made up by the aforementioned substitution.

Chromium. Chromium is concentrated in the early differentiates of igneous rocks, where it occurs in spinels, and in some of the silicates. In spite of the fact that it shows a much greater preference for pyroxene than for any associated

Table 14. Chromium in mafic igneous rocks (p.p.m.)

Chromium		Rock range	Reference
Aver.	Range		
340		Gabbro	GOLDSCHMIDT (1937a)*
410		Gabbro and dolerite	SAHAMA (1945)*
220	36-7700	59 Diabases, Ontario	FAIRBAIRN <i>et al.</i> (1953)
593	110-1100	3 Duluth gabbros	FAIRBAIRN <i>et al.</i> (1953)
466	400-500	3 Hawaiian basalts	WAGER and MITCHELL (1953)
121	nil-350	6 Skaergaard gabbros	WAGER and MITCHELL (1951)
733	300-2500	6 Gabbros and norites	NOCKOLDS and MITCHELL (1948)
166	84-300	19 Keweenawan basalts	CORNWALL and ROSE (1947) p. 213
350	60-900	5 Ontario norites	FRIEDMAN (1957) p. 1560

* From RANKAMA and SAHAMA (1950) p. 121

olivine (WAGER and MITCHELL, 1951, p. 183; CORNWALL and ROSE, 1957, p. 215). GOLDSCHMIDT (1954, p. 548) says it is most abundant in olivine rocks. In the silicates, chromium exists as Cr^{3+} and exhibits diadochous replacement with Fe^{3+} and Al^{3+} (RANKAMA and SAHAMA, 1950, p. 622).

In the Duluth complex as well as elsewhere, pyroxene shows a much higher concentration of chromium than does the associated olivine (Table 15). However, chromium in the pyroxenes of the olivine-free rocks averages somewhat lower than in the pyroxenes as a whole.

Table 15. Cr_2O_3 in minerals (p.p.m.)

Location	Olivine		Pyroxene	
	Aver.	Range	Aver.	Range
Ham-Brule	35	6-170	354	10-1300
Kawishiwi	58	5-230	580	35-1500
Skaergaard*	10	nil-20	1117	nil-3000
Greenstone†	5	0-9	321	5-1200

* Recalculated to Cr_2O_3 from columns A, B, and C (less iron-rich gabbros), Table B, WAGER and MITCHELL (1951).

† Recalculated to Cr_2O_3 from CORNWALL and ROSE (1957) p. 215.

In the Kawishiwi traverse olivines, Cr^{3+} increases generally upward, with a pronounced enrichment in the uppermost three samples (Fig. 18). It is thus concentrated in the magnesium-rich varieties, as has been found in other areas (WAGER and MITCHELL, 1951, p. 183). In both the pyroxenes and olivines of the Ham-Brule traverse, Cr^{3+} shows considerable local fluctuation but no major trends (Fig. 19).

On the basis of ionic radius and electronegativity, Cr^{3+} would be expected to proxy more readily for Fe^{3+} than for Al^{3+} . The lower electronegativity of Cr^{3+} with respect to Fe^{3+} should result in its enrichment in the crystal phase, which is the common situation (RINGWOOD, 1955, p. 199). GOLDSCHMIDT (1954, p. 549) has suggested that divalent chromium may be present in some of the pyroxenes. If this is true, it should replace either Fe^{2+} or Mg^{2+} . The generally recognized concentration of chromium in magnesium-rich rocks and minerals suggests that Cr^{2+} - Mg^{2+} diadochy may take place.

Vanadium. In igneous rocks, vanadium occurs in three stable oxidation states, viz. as V^{3+} , V^{4+} , and V^{5+} . In the early and intermediate stages it is dominantly present in the trivalent form according to GOLDSCHMIDT (1954, p. 489). Like chromium, its neighbour in the periodic table, it is a characteristic constituent of magnetite and pyroxene, but not so much of olivine (WAGER and MITCHELL, 1951, p. 185). GOLDSCHMIDT considers V^{3+} to be closely related to Cr^{3+} and Fe^{3+} (1954, p. 487). RANKAMA and SAHAMA on the other hand, point out that V^{3+} is a strong reducing agent which, if present, should reduce ferric iron to the ferrous state. They consider V^{4+} to be more plentiful in igneous rocks and to replace Ti^{4+} , Fe^{3+} , and Al^{3+} (RANKAMA and SAHAMA, 1950, p. 596).

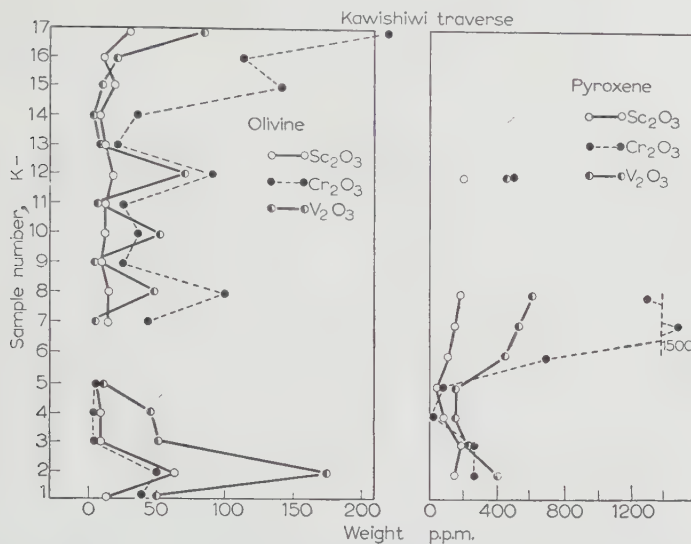


Fig. 18. Distribution of Sc_2O_3 , Cr_2O_3 and V_2O_3 in the olivines and pyroxenes of the Kawishiwi traverse.

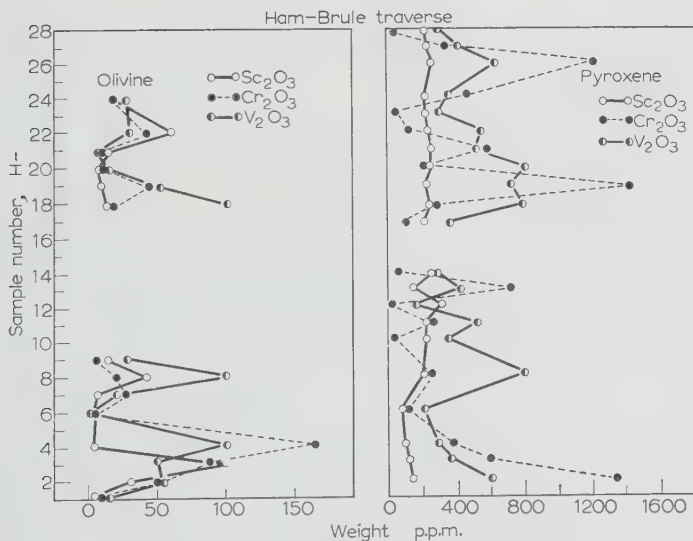


Fig. 19. Distribution of Sc_2O_3 , Cr_2O_3 and V_2O_3 in the olivines and pyroxenes of the Ham-Brule traverse.

Table 16. Vanadium in mafic igneous rocks (p.p.m.)

Vanadium		Rock type	Reference
Aver.	Range		
56		Gabbros and dolerites	SAHAMA (1945)*
320		Basic rocks, Sweden	LUNDEGÅRDH (1946)*
254	150-500	6 Skaergaard gabbros	WAGER and MITCHELL (1951)
283	200-400	3 Hawaiian basalts	WAGER and MITCHELL (1953)
220	120-430	58 Ontario diabases	FAIRBAIRN <i>et al.</i> (1953)
183	100-280	3 Duluth gabbros	FAIRBAIRN <i>et al.</i> (1953)
165		Sudbury norite, av.	STONEHOUSE (1954)
100	100-100	5 Ham-Brule trav. gabbros	This study
141	50-250	6 Gabbros and norites	NOCKOLDS and MITCHELL (1948)
188	120-300	19 Keweenawan basalts	CORNWALL and ROSE (1957)
78	30-160	6 Norites, Ontario	FRIEDMAN (1957)

* Taken from RANKAMA and SAHAMA (1950) p. 596.

Vanadium content of a number of basic igneous rocks is given in Table 16. The five rocks from this study are comparable in vanadium to those from other areas.

Table 17 is a comparison of the V_2O_3 content of olivine and pyroxene from the two Duluth traverses with its occurrence in the same minerals from other igneous bodies. In all the Duluth minerals, the V_2O_3 shows good correlation with that of Cr_2O_3 (Figs. 18 and 19). In the Ham-Brule olivines, V_2O_3 shows good correspondence with TiO_2 as well. As vanadium is known to be concentrated in titaniferous iron ores (RANKAMA and SAHAMA, 1950, p. 595), the close association between V_2O_3 and TiO_2 (Figs. 19 and 16) in the Ham Brule traverse olivines suggests that both these elements are present in magnetite or ilmenite impurities, especially as any vanadium present in the olivines of the Skaergaard intrusion was below the limit of sensitivity.

The correspondence between the distribution of vanadium and chromium in both pyroxenes and olivines may be readily seen (Figs. 18 and 19). This relationship suggests that the vanadium is present as V^{4+} , whose radius and electronegativity are the same as those of Cr^{3+} . The vanadium/chromium ratio was found to remain relatively constant.

Table 17. V_2O_3 in minerals (p.p.m.)

Location	Olivine		Pyroxene	
	Aver.	Range	Aver.	Range
Ham-Brule	41	10-100	410	100-780
Kawishiwi	36	5-180	305	100-500
Skaergaard*		trace	383	178-622
Greenstone†	53	36-71	630	71-1230

* Recalculated to V_2O_3 from columns A, B, and C (less iron-rich gabbros), Table B, WAGER and MITCHELL (1951).

† Recalculated to V_2O_3 from CORNWALL and ROSE (1957) p. 215.

Table 18. Scandium in mafic igneous rocks (p.p.m.)

Scandium		Rock type	Reference
Aver.	Range		
30		Gabbro, average	GOLDSCHMIDT (1954)
20		Gabbro and dolerite	SAHAMA (1945)*
13	nil-30	6 Skaergaard gabbros	WAGER and MITCHELL (1951)
10	10-10	3 Hawaiian basalts	WAGER and MITCHELL (1953)
37	21-61	59 Ontario diabases	FAIRBAIRN <i>et al.</i> (1953)
25	21-33	3 Duluth gabbros	FAIRBAIRN <i>et al.</i> (1953)
22	10-40	6 Gabbros and norites	NOCKOLDS and MITCHELL (1948)

* From RANKAMA and SAHAMA (1950) p. 516.

The distribution curves for V_2O_3 in the pyroxenes are similar to those of CaO (Figs. 18 and 5; 19 and 4). As the CaO content is primarily a function of the ortho- to clinopyroxene ratio, it may be that vanadium is concentrated in the clinopyroxenes, where it substitutes for Fe^{3+} or Al^{3+} but is not present to any extent in the orthopyroxenes.

Scandium. Scandium, long considered one of the rarest of elements, is now known to have a wide distribution in rocks and minerals. It occurs as Sc^{3+} in early formed ferromagnesian minerals, and probably replaces Mg^{2+} or Fe^{2+} (GOLDSCHMIDT, 1954, p. 304), but not Ca^{2+} , Fe^{3+} or Al^{3+} because of the large differences in radii (RANKAMA and SAHAMA, 1950, p. 513). WAGER and MITCHELL (1951, p. 192), however, suggest that scandium may occupy the Ca^{2+} position in pyroxenes, the mineral group in which it is most abundant.

The scandium content of basic rocks from a number of areas is shown in Table 18. Like vanadium and chromium, scandium is concentrated in the pyroxenes. GOLDSCHMIDT (1954, p. 305) gives the following average values: olivine, 11 p.p.m. Sc_2O_3 ; and pyroxene, 152 p.p.m. Sc_2O_3 . These values may be compared with Table 19.

In the olivines of the Duluth gabbro, the Sc_2O_3 curves (Figs. 18 and 19) correlate with those of V_2O_3 and Cr_2O_3 . In the pyroxenes of the Ham-Brule traverse, Sc_2O_3 shows a very similar trend to CaO (Figs. 19 and 4) which lends support to the contention of WAGER and MITCHELL that Sc^{3+} may substitute for Ca^{2+} in the pyroxene structure.

Table 19. Sc_2O_3 in minerals (p.p.m.)

Location	Olivine		Pyroxene	
	Aver.	Range	Aver.	Range
Ham-Brule	24	6-100	167	50-350
Kawishiwi	17	3-70	120	50-180
Skaergaard*		trace	78	45-120
Greenstone†	15	15-15	262	120-300

* Recalculated to Sc_2O_3 from columns A, B, and C (less iron-rich gabbros), Table B, WAGER and MITCHELL (1951).

† Recalculated to Sc_2O_3 from CORNWALL and ROSE (1957) p. 215.

SUMMARY AND CONCLUSIONS

The element distribution in the olivines, pyroxenes and feldspars from these two traverses may be summarized as follows: Along the Kawishiwi traverse, the MgO, NiO and Cr_2O_3 of the olivines show a progressive increase upward, whereas the FeO, MnO, CoO, CuO and ZrO_2 decrease upward, and the TiO_2 , V_2O_5 and Sc_2O_3 exhibit no consistent trend. In order to determine the significance of these apparent trends, correlation coefficients for all the analysed components of the Kawishiwi olivines were calculated (Table 20). Probability of significance values

Table 20

Oxide	Correlation coefficient (%)	Probability of significance (%)
MnO	85.3	99.9 +
FeO	83	99.9 +
CuO	71.7	99.9
CoO	50	96
ZrO_2	36	<90
TiO_2	14.7	<90
NiO	12	<90
CaO	5.5	<90
Sc_2O_3	15.4	<90
Cr_2O_3	59.5	97
MgO	84	99.9 +

were determined from the correlation coefficients. These values simply tell what the chances are that there is some relationship between the amount of oxide and its position in the traverse. Thus, there are over 999 chances out of 1000 that the MnO in the Kawishiwi olivines actually does decrease upward, and less than one chance in 1000 that this distribution could have resulted from sampling of a random population. If 95 per cent is taken as the significance limit, the MnO, FeO, CuO, CoO, Cr_2O_3 and MgO show a definite relationship between amount and location in the traverse.

The Kawishiwi samples for which there are analysed pyroxenes come, with one exception, from the lower part of the traverse, and these pyroxenes are too few in number to show significant trends. They tend to be higher than their associated olivines in the elements scandium, vanadium and chromium, whereas they have roughly equivalent amounts of zirconium, titanium, copper and manganese, and are somewhat lower in nickel and cobalt. Essentially similar relationships hold between the olivines and pyroxenes of the Ham-Brulé traverse.

The most significant trend shown by the Kawishiwi feldspars is the upward increase in the anorthite content which corresponds with increasing forsterite in the olivines (Fig. 6). As the correlation coefficient for this trend in the feldspars is 17.5 per cent, there are approximately eight chances in ten that this increase is significant.

As has been pointed out, the classic examples of large, differentiated, mafic bodies all have in common an upward increase of iron and decrease of magnesium in the olivines and pyroxenes and a corresponding increase in albite content of the plagioclases. The Duluth complex, on the other hand, shows just the opposite

Table 21. Chemical analyses of five Ham-Brule traverse rocks

Component	H-1 (pct.)	H-9 (pct.)	H-18 (pct.)	H-19 (pct.)	H-21 (pct.)
SiO ₂	48.23	47.18	45.05	45.88	47.42
TiO ₂	0.88	1.00	3.60	1.52	2.32
Al ₂ O ₃	20.05	22.13	18.35	15.96	15.37
Fe ₂ O ₃	1.57	1.72	0.14	2.22	1.35
FeO	9.20	8.81	13.00	11.64	11.52
MgO	6.03	4.99	5.39	9.33	7.43
CaO	8.58	9.19	9.73	9.39	9.19
Na ₂ O	3.18	3.69	2.97	2.44	2.84
K ₂ O	1.01	0.63	0.51	0.63	0.63
MnO	0.18	0.12	0.22	0.23	0.19
CO ₂	0.33	0.33	0.43	0.37	0.31
BaO	0.03	0.03	0.03	0.03	
Li ₂ O	0.10	0.12	0.14	0.10	0.10
P ₂ O ₅	0.21	0.09	0.19	0.14	0.37
V ₂ O ₅	0.02	0.02	0.02	0.02	0.02
H ₂ O	0.61	trace	0.10	0.60	0.54
Ni	0.04	0.04	0.04	0.03	0.07
S	0.03	0.02	0.02	0.04	0.03
Total	100.28	100.11	99.93	100.57	99.70

W. C. BOWDEN, Ledoux and Company, analyst.

H-1—Olivine gabbro containing 25% olivine (Fa₄₇), 9% clinopyroxene, 65% plagioclase (An₅₇) and <1% magnetite, biotite, zircon and serpentine.

H-9—Olivine gabbro containing 15% olivine (Fa₄₉), 8% subcalic augite, 72% plagioclase (An₆₆) and 5% magnetite biotite.

H-18—Olivine norite containing 25% olivine (Fa₆₃), 6% hypersthene, 60% plagioclase (An₆₂), 8% magnetite and <1% biotite, apatite and chlorite.

H-19—Olivine gabbro containing 20% olivine (Fa₄₂), 16% augite, 60% plagioclase (An₆₈), and 4% magnetite + biotite.

H-21—Olivine gabbro containing 17% olivine (Fa₅₆), 16% augite + hypersthene, 60% plagioclase (An₅₇) and 7% magnetite.

All percentages are based on visual estimation from thin section. Fa content based on average of spectrographic and index oil determinations. An content based on index oil determination.

trends along the Kawishiwi traverse. In addition, significant variations in the trace elements of the olivines are just reversed from what would be expected in a normally-differentiated body. Samples from the Ham-Brule traverse, which is about 50 miles to the east, do not exhibit any recognizable trends. They show instead marked local fluctuations in mineral percentage and composition.

Although the samples from the Duluth complex are too few and too localized to be in any way definitive, the reversed trends in the Kawishiwi olivines and feldspars do require some kind of explanation. One possibility is that the present

Table 22. Some major and trace constituents in olivines from the Kawishiwi traverse

Sam- ple	FeO*	MgO	CaO	MnO	NiO	CoO	CuO	ZrO ₂	TiO ₂	Cr ₂ O ₃	V ₂ O ₃	Sc ₂ O ₃
K-1	34.2	26	0.2	0.47	1000	400	520	180	1.15	40	x	20
K-2	37.3	20	0.7	0.7	1000	320	700	380	0.5	50	x	20
K-3	36.0	23.5	0.2	0.6	1500	420	550	190	0.25	10	x	15
K-4	39.3	19.5	0.2	0.65	1200	360	260	250	0.55	12	x	15
K-5	38.6	22	0.25	0.5	1100	360	260	120	0.4	5	x	5
K-7	32.2	26	0.3	0.45	1200	350	95	120	0.23	40	x	20
K-8	30.9	28	0.6	0.45	1000	420	390	130	0.17	100	x	17
K-9	32.2	27	0.2	0.45	1100	320	10	100	0.75	20	x	6
K-10	32.2	28	0.1	0.45	1250	320	10	100	0.19	25	x	10
K-11	32.2	28	0.1	0.5	800	400	35	120	0.3	20	x	10
K-12	29.6	26	0.75	0.45	800	350	120	100	0.9	85	x	20
K-13	33.5	27	0.2	0.45	1300	330	80	130	0.16	12	x	6
K-14	27.0	34	0.15	0.35	1150	400	65	90	0.05	23	x	3
K-15	23.2	35	0.5	0.32	2300	320	200	90	0.095	140	x	22
K-16	21.9	34	0.35	0.33	2900	300	25	80	0.2	110	x	10
K-17	27.0	36	0.18	0.35	2400	270	150	120	1.2	230	x	25

* FeO recalculated from total Fe.

FeO, MgO, CaO, MnO and TiO₂ values are present in weight per cent. All others in p.p.m. by weight.

OIVA JOENSUU, analyst.

x—present in amounts <10 p.p.m.

Table 23. Some major and trace constituents in pyroxenes from the Kawishiwi traverse

Sam- ple	FeO*	MgO	CaO	MnO	NiO	CoO	CuO	ZrO ₂	TiO ₂	Cr ₂ O ₃	V ₂ O ₃	Sc ₂ O ₃
K-2	20.6	16	12	0.5	500	140	160	330	0.75	310	90	150
K-3	24.5	22	3.1	0.52	450	210	540	160	0.3	290	30	180
K-4	27.7	20	1.7	0.6	670	210	270	200	0.6	35		55
K-5	25.8	19	1.4	0.5	450	200	270	240	0.32	60	20	50
K-6	12.8	14	15	0.27	350	100	550	290	1.5	700	80	100
K-7	13.5	17.5	14	0.25	240	100	90	150	0.92	1500	35	120
K-8	13.5	17	14	0.3	220	105	90	190	0.9	1300	45	150
K-12	17.4	19	12.5	0.4	500	120	170	250	0.7	300	25	160

* FeO recalculated from total Fe.

FeO, MgO, CaO, MnO and TiO₂ values are in weight per cent. All others in p.p.m. by weight.

OIVA JOENSUU, analyst.

Table 24. Some major and trace constituents in feldspars from the Kawishiwi traverse

Sample	CaO	Na ₂ O	K ₂ O	FeO*	MgO	MnO	NiO	CoO	CuO	TiO ₂
K-1	11	4.6	0.5	0.64	0.3	100	25	x	80	0.095
K-2	11	4.7	0.6	0.48	0.14	70	8	x	45	0.08
K-3	11.5	4.7	0.55	0.49	0.14	70	15	x	80	0.095
K-4	11.5	4.6	0.55	0.40	0.09	50	5	x	60	0.075
K-5	11	4.7	0.65	0.39	0.09	65	5	x	30	0.07
K-6	11	4.6	0.95	0.73	0.38	120	10	x	25	0.075
K-7	11.2	4.6	0.5	0.50	0.22	64	8	x	30	0.08
K-8	11.2	4.7	0.5	0.52	0.13	62	3	x	20	0.09
K-9				0.64	0.22	90	5	x	70	0.105
K-10				0.53	0.25	80	5	x	20	0.095
K-11				0.52	0.18	75	3	x	35	0.1
K-12	12	4.65	0.45	0.54	0.22	85	3	x	50	0.13
K-13	12	4.6	0.40	0.57	0.47	150	7	x	20	0.095
K-14				0.54	0.19	70	5	x	15	0.105
K-15	11.5	3.7	0.4	0.71	0.95	230	12	x	20	0.088
K-16				0.71	0.85	150	20	x	15	0.07
K-17	12.2	3.7	0.47	0.77	0.85	250	25	x	30	0.088

* FeO recalculated from total Fe.

MnO, NiO, CoO, and CuO values are in p.p.m. by weight. All others in weight per cent.

OIVA JOENSUU, analyst.

x—present in amounts less than 5 p.p.m.

Table 25. Some major and trace constituents in olivines from the Ham-Brulé traverse

Sample	FeO*	MgO	CaO	MnO	NiO	CoO	CuO	ZrO ₂	TiO ₂	Cr ₂ O ₃	V ₂ O ₃	Sc ₂ O ₃
H-1	38.5	23	0.15	0.55	1300	300	130	100	0.15	10	10	6
H-2	37	25	0.8	0.5	1100	400	200	100	0.34	50	55	35
H-3	37	25	0.3	0.5	900	380	150	100	0.24	70	50	100
H-4	38.5	25	0.25	0.6	620	200	250	100	1.1	170	100	10
H-6	40	25	0.15	0.6	600	350	40	100	0.12	10	10	10
H-7	35	24.5	0.1	0.48	800	500	130	100	0.2	25	20	10
H-8	35	25.5	0.35	0.57	650	350	1200	100	1.2	20	100	40
H-9	42.5	23.5	2.5	0.57	800	270	620	100	0.18	12	20	15
H-18	47.5	15	0.4	1.0	270	230	500	100	1.3	20	100	15
H-19	35	28	0.7	0.52	1200	300	50	100	0.15	45	60	10
H-20	36	24	0.35	0.66	1100	310	110	100	0.1	10	10	10
H-21	42.5	18.5	0.25	0.77	550	270	350	100	0.17	10	10	10
H-22	37	17	1.1	0.72	390	270	350	100	0.35	35	25	60

* FeO recalculated from total Fe.

FeO, MgO, CaO, MnO and TiO₂ values are in weight per cent. All others in p.p.m. by weight.

OIVA JOENSUU, analyst.

igneous mass resulted from multiple injection. Assume that normal differentiation by means of crystal settling took place in a large body of simatic magma, possibly in a chamber beneath the present site of Lake Superior. At some time after the crystallization and settling of the early-formed peridotites and chromitites, some of this magma was injected into the unconformity between the Keweenaw flows and the older formations, and these injections were repeated at intervals thereafter.

Table 26. Some major and trace constituents in pyroxenes from the Ham-Brule traverse

Sam- ple	FeO*	MgO	CaO	MnO	NiO	CoO	CuO	ZrO ₂	TiO ₂	Cr ₂ O ₃	V ₂ O ₃	Sc ₂ O ₃
H-2	14	16	18	0.32	250	90	120	220	0.78	1300	620	160
H-3	17.5	18	11	0.36	250	90	350	230	0.55	600	350	125
H-4	20.5	19	6	0.45	180	120	180	110	0.6	350	300	70
H-6	25	21	2.5	0.55	200	100	200	170	0.34	80	190	50
H-8	13.5	14.5	19.5	0.3	120	80	560	125	0.73	230	780	190
H-10	18.5	11	15	0.35	100	100	900	400	0.93	35	300	190
H-11	15	12	17.5	0.4	100	80	180	120	0.95	200	490	190
H-12	18	11	19.5	0.5	12	50	55	130	0.52	10	100	300
H-13	26	19	3	0.55	270	80	160	200	0.44	700	410	150
H-14	18.5	10	19.0	0.5	200	60	420	150	0.78	35	200	200
H-17	17	11.5	19.5	0.47	60	70	330	150	1.1	140	300	180
H-18	16.7	12	17.5	0.4	70	80	150	130	1.05	230	750	200
H-19	11	14.5	17	0.25	400	80	100	100	1.0	1300	630	170
H-20	13	14	17	0.3	300	70	100	150	1.25	180	750	190
H-21	14	14	13	0.37	220	100	220	100	1.05	550	440	200
H-22	14	12.5	16.5	0.35	150	90	180	180	0.6	30	450	170
H-23	18.5	11.5	13.5	0.45	300	80	900	150	1.05	10	230	160
H-24	15.5	19.5	9.5	0.35	300	130	180	150	0.6	420	310	150
H-25	14.5	15	17.5	0.33	200	90	100	110	1.0	1200	630	190
H-27	16	13	17.5	0.4	140	90	350	170	0.85	300	340	170
H-28	16	11	0.19	0.42	30	70	80	220	1.35	10	200	150

* FeO recalculated from total Fe.

FeO, MgO, CaO, MnO, and TiO₂ values are in weight per cent. All others in p.p.m. by weight.
OIVA JOENSUU, analyst.

In the region of the Ham-Brule traverse, the injections intruded one another, thereby giving rise to large local variations in mineral and trace element composition. In the area of the Kawishiwi traverse, however, each injection solidified to such an extent that subsequent surges could not penetrate and were forced to spread out laterally immediately beneath, thereby giving the youngest rocks at the bottom and an apparent reversal of the differentiation trend.

Support for this hypothesis is found in areas other than the two from which samples were taken. At Duluth, Minnesota, TAYLOR (1956, p. 42) has found cross-cutting relationships within the layered series of the complex. One separate intrusion, called the Bardon's Peak gabbro, has been injected into the older gabbro but without any chilling effects, indicating that the two intrusions were nearly contemporaneous.

BLACKADAR (1956) describes a somewhat similar situation in some of the Logan sills associated with the Duluth complex. On the basis of petrographic studies and chemical analyses, he found most of these sills to fluctuate erratically upward with regard to mineral composition, grain size, etc. One sill even showed an upward decrease in the fayalite content of the olivines, similar to the trend along the Kawishiwi traverse. These phenomena he attributed to multiple injections from some distant magmatic reservoir.

Table 27. Some major and trace constituents in feldspars from the Ham-Brule traverse

Sample	CaO	Na ₂ O	K ₂ O	FeO*	MgO	MnO	NiO	CoO	CuO	TiO ₂
H-1	10.5	4.65	0.65	0.80	0.53	130	25	x	130	0.09
H-2	11.5	4.8	0.5	0.71	0.35	100	8	3	35	0.105
H-3	11	4.95	0.55	0.67	0.35	85	9	x	60	0.11
H-4	12	4.90	0.6	0.97	0.5	110	25	5	100	0.045
H-5	9.5	5.15	1.5	1.13	0.45	50	16	10	15	0.12
H-6	11.5	4.7	0.55	0.90	0.45	140	10	5	65	0.12
H-7	12	4.85	0.5	1.4	0.85	260	25	10	100	0.12
H-8	11	5.25	0.50	0.68	0.3	100	10	x	220	0.11
H-9	11	4.85	0.65	0.54	0.21	90	10	x	50	0.08
H-10	9	4.7	1.8	1.13	0.45	160	3	x	60	0.072
H-11	11.5	5.07	0.5	0.58	0.16	100	x	x	60	0.10
H-12	8	5.13	2.2	0.58	0.21	160	x	x	10	0.05
H-13	11	5.25	0.5	0.84	0.4	250	40	5	130	0.12
H-14	9	5.3	0.62	0.54	0.08	90	x	x	50	0.065
H-15	9.5	5.25	1.18	0.97	0.28	160	x	x	80	0.075
H-16	8	4.65	3.0	0.80	0.45	95	22	x	10	0.065
H-17	12	4.7	0.6	0.71	0.15	95	x	x	50	0.085
H-18	11	3.05	0.4	0.90	0.27	100	x	x	110	0.095
H-19	11.5	4.15	0.5	1.55	0.9	210	70	10	120	0.13
H-20	12.5	4.3	0.42	0.97	0.45	110	20	3	130	0.11
H-21	10	5.2	0.85	0.81	0.25	100	25	5	180	0.085
H-22	10	5.4	0.7	0.73	0.21	110	15	8	130	0.1
H-23	8.5	5.85	1.2	1.68	1.0	240	25	10	130	0.22
H-24	12.7	3.85	0.35	1.13	0.9	170	12	x	40	0.09
H-25	10	4.75	0.55	0.71	0.25	90	20	8	90	0.08
H-26	11.5	4.6	0.42	1.3	0.65	165	30	10	120	0.09
H-27	10.5	5.15	0.7	1.3	0.25	230	25	12	40	0.095
H-28	8	5.25	1.75	1.2	0.22	200	x	x	10	0.095

* FeO recalculated from total Fe.

MnO, NiO, CoO, and CuO values are in p.p.m. by weight. All others in weight per cent.

x—present in amounts of <3 p.p.m.

OIVA JOENSUU, analyst.

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REFERENCES

- BAYLEY W. S. (1893) The basic massive rocks of the Lake Superior region. *J. Geol.* **1**, 435-596, 688-716.
- BLACKADAR R. G. (1956) Differentiation and assimilation in the Logan sills, Lake Superior district, Ontario. *Amer. J. Sci.* **254**, 623-645.
- CORNWALL H. R. (1951) Differentiation in lavas of the Keweenaw series and the origin of the copper deposits of Michigan. *Bull. Geol. Soc. Amer.* **62**, 159-202.
- CORNWALL H. R. and ROSE H. J., JR. (1957) Minor elements in Keweenaw lavas, Michigan. *Geochim. et Cosmochim. Acta* **12**, 209-224.
- DALY R. A. (1928) The Bushveld igneous complex of the Transvaal. *Bull. Geol. Soc. Amer.* **39**, 703-768.
- DEGENHARDT H. (1957) Untersuchungen zur geochemischen Verteilung des Zirkoniums in der Lithosphäre. *Geochim. et Cosmochim. Acta* **11**, 279-309.
- FAIRBURN H. W., AHRENS L. H. and GORFINKLE L. G. (1953) Minor element content of Ontario diabase. *Geochim. et Cosmochim. Acta* **3**, 34-46.
- FRIEDMAN G. M. (1957) Structure and Petrology of the Caribou Lake intrusive body, Ontario, Canada. *Bull. Geol. Soc. Amer.* **68**, 1531-1564.
- GOLDSCHMIDT V. M. (1937) The principles of distribution of chemical elements in minerals and rocks. *J. Chem. Soc.* 655.
- GOLDSCHMIDT V. M. (1954) *Geochemistry*. Clarendon Press, Oxford.
- GREEN J. (1953) Geochemical Table of the elements. *Bull. Geol. Soc. Amer.* **64**, 1001-1012.
- GROSH W. A., PENNINGTON J. W., WASSON P. A. and COOKE S. R. B. (1955) Investigation of copper-nickel mineralization in Kawishiwi River area, Lake County, Minnesota. *Bur. Mines Report of Investigations* 5177.
- GROUT F. F. (1918a) The lopolith, an igneous form exemplified by the Duluth gabbro. *Amer. J. Sci.* Ser. 4, **46**, 516-522.
- GROUT F. F. (1918b) A type of igneous differentiation. *J. Geol.* **26**, 626-658.
- GROUT F. F. (1918c) The pegmatites of the Duluth gabbro. *Econ. Geol.* **13**, 185-197.
- GROUT F. F. (1926) Internal structures of igneous rocks with special reference to the Duluth gabbro. *J. Geol.* **26**, 439-458.
- HOWLAND A. L., PEOPLES J. W. and SAMPSON E. (1936) The Stillwater igneous complex and associated occurrences of nickel and platinum group metals. *Montana Bur. Mines and Geol. Misc. Contribution* 7.
- LUNDEGÅRDH P. H. (1946) Rock composition and development in Central Roslagen, Sweden. *Ark. Kemi. Min. Geol. A* **23** No. 9, 1-160.
- MASON B. (1952) *Principles of Geochemistry*. Wiley, New York.
- NEBEL M. L. (1919) Basal phases of the Duluth gabbro. *Econ. Geol.* **14**, 367-402.
- NOCKOLDS S. R. and MITCHELL R. L. (1948) The geochemistry of some Caledonian plutonic rocks: a study in the relationship between major and trace elements of igneous rocks and their minerals. *Trans. Roy. Soc. Edinb.* **61**, 533-575.
- POLDERVAART A. (1956) Zircon in rocks. II: Igneous rocks. *Amer. J. Sci.* **254**, 521-554.
- RAMBERG H. (1952) Chemical bonds and distribution of cations in silicates. *J. Geol.* **60**, 331-355.
- RANKAMA K. and SAHAMA T. G. (1950) *Geochemistry*. The University of Chicago Press.
- RINGWOOD A. E. (1955) The principles governing trace element distribution during magmatic crystallization. *Geochim. et Cosmochim. Acta* **7**, 189-202; 242-254.
- SAHAMA T. G. (1945) Spurenelemente der Gesteine im südlichen Finnisch-Lapland. *Bull. Comm. Géol. Fin.* No. 135.
- SANDELL E. B. and GOLDICH S. S. (1943) The rarer metallic constituents of some American igneous rocks. *J. Geol.* **51**, 99-115, 167-189.
- SCHWARTZ G. M. and DAVIDSON D. M. (1952) Geologic setting of the copper-nickel prospect in the Duluth gabbro near Ely, Minnesota. *Mining Engr.* 699-702.
- STONEHOUSE H. B. (1954) An association of trace elements and mineralization Sudbury. *Amer. Min.* **39**, 452-474.
- STORM T. W. and HOLLAND H. D. (1957) The distribution of nickel in the Lambertville diabase. *Geochim. et Cosmochim. Acta* **11**, 335-347.

- TAYLOR R. B. (1956) *The Duluth Gabbro Complex, Duluth, Minnesota: Precambrian of Northeastern Minnesota*. Guidebook, Ann. meeting of Geol. Soc. Amer. Minneapolis, Minnesota.
- VOGT J. H. L. (1923) Nickel in igneous rocks. *Econ. Geol.* **18**, 307-353.
- WAGER L. R. and DEER W. A. (1939) The petrology of the Skaergaard intrusion Kangerdlugssuaq, East Greenland. *Medd. Grønland* **105**, 1-352.
- WAGER L. R. and MITCHELL R. L. (1951) The distribution of trace elements during strong fractionation of basic magma—A further study of the Skaergaard intrusion, East Greenland. *Geochim. et Cosmochim. Acta* **1**, 129-208, 217-223.
- WAGER L. R. and MITCHELL R. L. (1953) Trace elements in a suite of Hawaiian lavas. *Geochim. et Cosmochim. Acta* **3**, 217-223.
- WAHLSTROM E. E. (1955) *Petrographic Mineralogy*. Wiley, New York.
- WELLS R. C. (1943) *Relative Abundance of Nickel in the Earth's Crust*. U.S. Geol. Survey Prof. Paper 205-A, 1-21.
- WINCHELL N. H. (1900) Mineralogy and petrology of Minnesota. *M. G. S. Final Report*, **5** 937-1006.
- WINCHELL N. H. and GRANT U. S. (1900) The petrographic geology of the crystalline rocks of Minnesota. *M. G. S. Final Report* **5**, 75-936.
- YATES A. B. (1948) Properties of the International Nickel Company of Canada. *Structural Geology of Canadian Ore Deposits* Chap. III, Pt. 7, pp. 596-617.

The geochemistry of tungsten, with special reference to the rocks of the Uganda Protectorate

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Abstract—In recent years the quality of the abundance data for many elements has improved considerably. One exception to this is the data for tungsten, which is still very sparse and contradictory in character. In this paper the use of a new photometric procedure for the determination of tungsten is described, and new abundance data presented. The sampling is restricted to a small area, but in spite of this limitation, the survey is considered to be of general interest to geochemists.

The distribution of tungsten in silicate rocks is shown to be positively skewed, and where sufficient numbers of determinations have been made, is shown to approximate to lognormal. A value of 1.4 p.p.m. is recommended for the terrestrial abundance of tungsten in granitic rocks: further work is required before the abundance values given for carbonate and other silicate rocks can be considered to be of general application. Regional bias of the distribution of this element in granitic rocks, and variation of tungsten content with age in the sedimentary rock systems have been recorded. These observations are considered in relation to the general geochemistry of tungsten and the distribution of this element in rock-forming minerals.

INTRODUCTION

THIS work is based upon the determination of tungsten in 273 samples of rocks and minerals from the Uganda Protectorate. The sampling is thus restricted to an area of 93,981 miles², an area similar in size to Great Britain. In spite of this limitation, this survey is considered to be of general interest to geochemists for the following reasons:

- (1) No systematic study has been undertaken of the geochemistry of this element.
- (2) Existing abundance data are contradictory and limited to few samples.
- (3) The number of samples and the area is large enough to be a reasonable approximation to a statistical sample of a part of the earth's crust.

KURODA and SANDELL (1954) reported that because of the sparse existing data on the abundance and distribution of molybdenum, and the contradictory character of some of the results, they considered it worth while to investigate the geochemistry of this element in considerable detail. These remarks of KURODA and SANDELL with regard to molybdenum are even more applicable to the geochemistry of tungsten, for which the data available is both more sparse and more contradictory. For example, after quoting the abundance data of HEVESY and HOBIE (1933) for tungsten in igneous rocks, GOLDSCHMIDT (1954) reports: "... results seem to be fairly high and may later be subjected to reduction." RANKAMA and SAHAMA (1949) report "... the abundance values given ... are only tentative". The only recorded abundance value for tungsten in sediments is that of WILSON and FIELDER (1944) who reported 1-2 p.p.m. of tungsten as the normal content of a schist. No details are available of any previously reported

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determinations of tungsten in carbonate rocks. The work detailed in this paper was undertaken to supply some of this basic abundance data, and to provide a geochemical background for studies of tungsten ore genesis.

ANALYTICAL METHOD

All the determinations were made using a spectrophotometric method based upon earlier work (JEFFERY, 1956). In the procedure previously described, a preliminary separation of molybdenum and tungsten was made by extraction of the complexes with α -benzoinoxime. This was followed by photometric measurement of the complexes with toluene-3:4-dithiol in light petroleum solution. In the routine examination of a large number of samples for tungsten only, it was found possible to shorten this procedure by dispensing with the preliminary separation with α -benzoinoxime and also to carry out the complex precipitation in weakly acid solution without removing silica.

Under these conditions molybdenum is partially precipitated and extracted. It is necessary therefore to apply a correction in the calculation of the results for that portion of the molybdenum which is extracted with the tungsten. This is done in a similar manner to that described (JEFFERY, 1957) for the somewhat similar problem of partial extraction of tungsten with complete extraction of molybdenum.

The procedure adopted is carried out as follows. An 0.5 g sample of the rock material is fused with 3 g of sodium carbonate in a platinum crucible. The melt is leached with water and the oxides of iron, etc., removed by filtration. Sufficient sulphuric acid is added to the filtrate to bring the pH of the solution to within the range 0.5–2. 3 ml of the toluene-3:4-dithiol solution, prepared according to the directions of ALLEN and HAMILTON (1952) are added and the solution allowed to stand for 1 hr at 97–100°C. The precipitated complexes of molybdenum and tungsten with the reagent are extracted into 5 ml of purified light petroleum and the optical densities of the organic solution at 630 m μ and 680 m μ measured. In the present work a Hilger and Watts "Uvispek" spectrophotometer was used. Apart from the interference from molybdenum for which a correction is applied, no element present in amounts likely to be encountered in silicate rocks interferes.

The precision of the method depends very largely upon the amount of molybdenum present in the sample. Under ideal conditions, i.e. in the complete absence of molybdenum, results can be duplicated to 0.2 p.p.m. in the concentration range 1–2 p.p.m., and to ± 10 per cent at higher concentrations. In the presence of molybdenum the precision is somewhat lower, particularly at low tungsten concentrations.

The method used for silicate rocks has also been employed for manganese minerals. For carbonate rocks and iron and titanium minerals a mixture of equal weights of sodium carbonate and borax glass was used as flux. The introduced boron does not interfere with the tungsten determination. For niobium and tantalum minerals the separation of tungsten using magnesia solution described by SCHOELLER (1937) was employed, prior to the formation and extraction of the complex with toluene-3:4-dithiol. In all the earth-acid mineral specimens examined, it was found necessary to repeat the fusion in order to obtain complete separation of the tungsten from the niobium and tantalum.

THE DISTRIBUTION AND ABUNDANCE OF TUNGSTEN

Rocks of granitic composition

The results obtained for the tungsten content of fifty-eight rocks of granitic composition are given in Table 1. In order to make the selection as representative

as possible, rocks of all types (granitic gneiss, mobilized granite, magmatic granite, etc.) from all parts of the country have been included. The average or arithmetic mean of all the results listed in this table is 2.1 p.p.m. If the specimens obtained from the mineralized area of Singo are omitted, the arithmetic mean is reduced to

Table 1. Tungsten in granitic rocks

Locality	W (p.p.m.)	Locality	W (p.p.m.)
G 1 Kigungu, Entebbe, Mengo	1.4	G 31 Kawungera, Singo, Mengo	4.5
G 2 Busika, Mengo	0.5	G 32 Kyenjojo, Toro	0.6
G 3 Lutete, Mengo	0.8	G 33 Matiri, Toro	0.3
G 4 Mayanja, Mengo	0.5	G 34 Nakaai Road, Toror,	
G 5 Bulyake, Mengo	1.9	Karamoja	0.5
G 6 Sebagala, Mengo	1.3	G 35 Kotido, Karamoja	0.6
G 7 Kilinya, Mengo	1.5	G 36 Toror Hills, Karamoja	0.2
G 8 Kyotera, Masaka	2.2	G 37 Kamacharkol, Karamoja	0.4
G 9 Kyotera, Masaka	1.5	G 38 Lokichar, Karamoja	1.1
G 10 Kajumba, Masaka	1.5	G 39 Theau, Karamoja	n.d.
G 11 Lunyo, Mbale	1.5	G 40 Loyoro, Karamoja	0.1
G 12 Buteba, Mbale	1.1	G 41 Katakwi, Teso	0.2
G 13 Kateti Ridge, Ankole	3.0	G 42 Mwiri, Teso	1.0
G 14 Kabali, Ankole	1.4	G 43 Soroti, Teso	0.7
G 14 Luganda, Ankole	3.1	G 44 Oboke, Lango	0.1
G 16 Rwendgando, Ankole	1.9	G 45 Apendi-atana, Lango	1.2
G 17 Hamuyaga, Ankole	3.3	G 46 Ajan River, Acholi	1.1
G 18 Ntabahara, Ankole	3.7	G 47 Ajan River, Acholi	2.3
G 19 Kabiro, Ankole	3.5	G 48 Atanga, Acholi	1.7
G 20 Rubanda, Kigezi	3.7	G 49 Nadiang, Acholi	1.7
G 21 Katimiro, Kigezi	1.3	G 50 Nadiang, Acholi	1.1
G 22 Mitano, Kigezi	3.1	G 51 Achar, Acholi	0.4
G 23 Kyamagoye, Kigezi	2.4	G 52 Otuombare, West Nile	0.2
G 24 Kyambamba, Kigezi	1.6	G 53 Adro, West Nile	1.5
G 25 Mubende Hill, Mubende	3.7	G 54 Eyoyi, West Nile	0.2
G 26 Bamba Hill, Singo, Mengo	2.6	G 55 Kula, West Nile	0.5
G 27 Nakibimba Hill, Singo,		G 56 Adrima, West Nile	1.1
Mengo	9.2	G 57 Ayawa, West Nile	1.2
G 28 Lubanyi, Singo, Mengo	7.7	G 58 Ombiodridrewa, West Nile	1.9
G 29 Mpologoma, Singo, Mengo	11.9		
G 30 Kyamekonya, Singo,			
Mengo	12.0		

n.d.—not detected

1.4 p.p.m., which figure may be adopted for the abundance of tungsten in the granitic rocks of the area.

Plotting these results as frequency histograms, Figs. 1(a) and 1(b), using both linear and geometric scales shows that the distribution is not normal, but approximates to lognormal. The geometric mean may therefore be regarded as a better measure of the most frequent observation than the arithmetic mean. DUROVIC

(1958) has however shown that in a true, continuous lognormal distribution the two values geometric mean and most frequent observation are not identical and that the former is always slightly greater than the latter. The geometric mean of the results listed is 1.2 p.p.m., and if the results from the Singo area are excluded this value falls to 1.0 p.p.m. The standard deviation λ , calculated on the basis of a

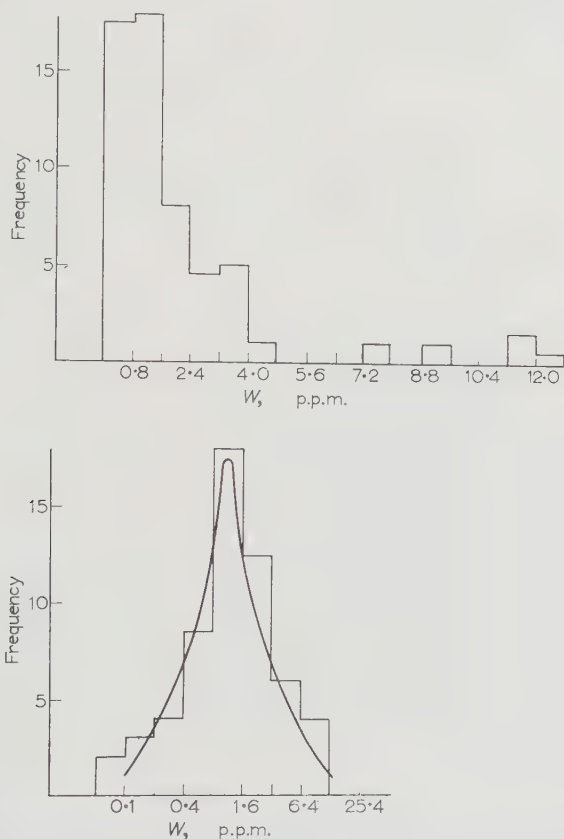


Fig. 1. Distribution of tungsten in rocks of granitic composition.
(a) 0.8 p.p.m. interval (b) $\times 2$ interval.

lognormal distribution is 0.49 (log). The antilog λ' , is 3.03, and hence it may be predicted that two-thirds of the total number of observations will fall in the range $1.2 \times 1/3.03$ to 1.2×3.03 , that is 0.4 to 3.7 p.p.m., which is in good agreement with the observed distribution.

Regional variation of the tungsten content of these rocks of granitic composition is shown in Table 2, where the results given in Table 1 have been grouped geographically. Any attempt to calculate an average value for the tungsten content of these rocks must therefore be based upon the examination of a truly representative selection of specimens. A similar variation to that illustrated in Table 2 has been shown to exist in the distribution of tungsten in the sediments and metasediments of the area (see below).

Table 2

Region	No. of samples	g.m. (p.p.m.)
Northern Uganda (Karamoja, Teso, Lango, Acholi, West Nile)	25	0.6
Masaka and Mengo (excluding Singo area)	10	1.2
Kigezi and Ankole	12	2.5
Singo	6	7.0

Table 3. Tungsten in basic rocks

Description and locality	W (p.p.m.)
B 1 Amphibolite, Entebbe, Mengo	6.3
B 2 Amphibolite, Jinja, Busoga	2.7
B 3 Amphibolite, Kanungu, Kigezi	3.2
B 4 Amphibolite, Wabusana, Mengo	4.3
B 5 Amphibolite, Bulola, Kigezi	3.4
B 6 Dolerite, Lwamajwa, Masaka	2.4
B 7 Dolerite, Nkulungu, Ankole	6.5
B 8 Dolerite, Nkulungu, Ankole	1.5
B 9 Dolerite, Rwanyamabale, Ankole	14.5
B 10 Dolerite, Aru, West Nile	0.9
B 11 Dolerite, Kasambya, Mubende	12.0

Table 4. Tungsten in alkali-rich rocks

Description and locality	W (p.p.m.)
A 1 Phonolite, Toror Hills, Karamoja	18.9
A 2 Phonolite, Toror Hills, Karamoja	23.7
A 3 Tinguaitite, Sukulu Hills, Mbale	0.4
A 4 Tinguaitite, Sagat, Karamoja	0.4
A 5 Nepheline-syenite, Sagat, Karamoja	0.7
A 6 Olivine-nephelinite, Napak, Karamoja	5.8
A 7 Melanephelinite, Napak, Karamoja	7.0
A 8 Melilite-nephelinite, Napak, Karamoja	17.0
A 9 Nephelinite, Napak, Karamoja	12.1
A 10 Phonolite, Napak, Karamoja	29.9
A 11 Pyroxenite, Elgon, Mbale	10.4
A 12 Trachyte, Toror Hills, Karamoja	5.8
A 13 Nephelinite, Toror Hills, Karamoja	11.7
A 14 Tinguaitite, Toror Hills, Karamoja	3.1
A 15 Tinguaitite, Toror Hills, Karamoja	14.8
A 16 Phonolite, Toror Hills, Karamoja	5.2
A 17 Phonolite, Toror Hills, Karamoja	3.7

Table 5. Tungsten in rocks of sedimentary origin

Description and locality		W (p.p.m.)	Description and locality		W (p.p.m.)
<i>Kaiso Beds</i>			<i>Mengo</i>		
SA 1	Shale, Mihbya, Toro	6.6	SG 9	Quartzite, Entebbe, Mengo	2.5
SA 2	Shale, Mihbya, Toro	4.7	SG 10	Quartzite, Kampala, Mengo	2.3
SA 3	Shale, Kibuku, Toro	4.9	SG 11	Mica-schist, Kampala, Mengo	4.8
SA 4	Shale, Kibuku, Toro	9.0	SG 12	Mica-schist, Mitala Maria, Mengo	1.8
SA 5	Mudstone, Kibuku, Toro	6.2	SG 13	Phyllite, Mabira, Mengo	1.9
<i>Kisegi Beds</i>			SG 14	Quartzite, Sezibwa, Mengo	10.4
SB 1	Sandstone, Kasunja, Toro	3.7	SG 15	Quartzite, Jinja, Busoga	9.8
SB 2	Sandstone, Kasunja, Toro	3.7	SG 16	Mudstone, Kibali Bridge, Masaka	6.8
SB 3	Siltstone, Kyoga, Toro	5.3			
<i>Karoo Beds</i>			SG 17	Phyllite, Kibali Bridge, Masaka	5.7
SC 1	Shale, Entebbe, Mengo	4.2	SG 18	Mudstone, Kinoni Hill, Masaka	3.6
SC 2	Shale, Entebbe, Mengo	2.6	SG 19	Phyllite, Bwiza Hill, Masaka	3.7
SC 3	Shale, Bugiri, Busoga	15.1	SG 20	Hornfels, Lwanda, Masaka	6.3
SC 4	Shale, Bugiri, Busoga	2.4	SG 21	Schist, Lwanda, Masaka	12.5
<i>Bukoban Series</i>			SG 22	Schist, Lwanda, Masaka	25.0
SD 1	Sandstone, Sango Hills, Masaka	5.5	SG 23	Phyllite, Kalongo, Masaka	4.0
<i>Singo Series</i>			SG 24	Phyllite, Lugaga, Ankole	3.6
SE 1	Siltstone, Bakijulula, Singo	1.8	SG 25	Phyllite, Gayaza, Ankole	5.0
SE 2	Sandstone, Kigalama, Singo	4.1	SG 26	Schist, Gayaza, Ankole	6.2
SE 3	Sandstone, Senda, Singo	33.8	SG 27	Phyllite, Nangura, Kigezi	5.8
SE 4	Sandstone, Lubona, Singo	1.2	SG 28	Phyllite, Kanungu, Kigezi	128.0
SE 5	Siltstone, Kimbeja Hill, Singo	50.7	SG 29	Phyllite, Kanungu, Kigezi	7.1
SE 6	Siltstone, Nsororo, Singo	7.0	SG 30	Quartzite, Kazumiro, Kigezi	33.8
<i>Bunyoro Series</i>			<i>Bulugwe Series</i>		
SF 1	Tillite, Kabwoya, Bunyoro	1.2	SH 1	Phyllite, Tororo, Mbale	0.3
SF 2	Shale, Isagara, Bunyoro	1.5	SH 2	Shale, Tororo, Mbale	2.2
SF 3	Shale, Kyamukama, Bunyoro	2.1	SH 3	Phyllite, Busia, Mbale	1.9
SF 4	Shale, Nyinana, Bunyoro	2.2	<i>Samia Series</i>		
SF 5	Siltstone, Lenji, Bunyoro	1.5	SJ 1	Shale, Amonikakine, Mbale	2.6
<i>Karagwe-Ankolean System</i>			SJ 2	Shale, Amonikakine, Mbale	3.4
SG 1	Phyllite, Kyesongera, Singo	15.7	SJ 3	Shale, Kami, Mbale	2.1
SG 2	Phyllite, Lukingiride, Singo	7.6	<i>Toro System</i>		
SG 3	Phyllite, Nabwendo Hill, Singo	8.9	SK 1	Sandy phyllite, Luhunga, Toro	n.d.
SG 4	Phyllite, Nsororo, Singo	89.9	SK 2	Phyllite, Nabohiki, Toro	1.0
SG 5	Phyllite, Kapeke, Singo	6.3	SK 3	Phyllite, Ntsinda, Toro	1.1
SG 6	Phyllite, Namatamba, Singo	28.5	SK 4	Schist, Kalebalena, Toro	2.9
SG 7	Quartzite, Mwezi, Singo	38.6	SK 5	Mudstone, Kabulasoke, Toro	4.3
SG 8	Mica-schist, Entebbe, Mengo	1.6	SK 6	Mica-schist, Kalulenze, Ankole	1.2

Table 5.—(contd.)

Description and locality	W (p.p.m.)	Description and locality	W (p.p.m.)
SK 7 Mica-schist, Nango, Ankole	1.6	SL 4 Quartzite, Moroto, Karamoja	n.d.
SK 8 Phyllite, Nango, Ankole	1.0	SL 5 Quartzite, Lotome, Karamoja	0.5
SK 9 Phyllite, Lubingo, Ankole	1.7	SL 6 Hornblende-quartzite, Kamion, Karamoja	0.2
<i>Basement Complex System</i>		SL 7 Quartz-mica-schist, Kitgum Acholi	3.1
SL 1 Quartzite, Ongbo, West Nile	0.5	SL 8 Garnet-schist, Kado River, Acholi	2.4
SL 2 Quartzite, Kucwiny, West Nile	0.8		
SL 3 Actinolite-schist, Ojio, West Nile	0.5		

n.d., not detected

Table 6. Graphitic phyllites from Ruhiza Mine

W (p.p.m.)							
No. 1	10	No. 11	17	No. 21	10	No. 31	12
No. 2	16	No. 12	34	No. 22	30	No. 32	24
No. 3	10	No. 13	23	No. 23	16	No. 33	27
No. 4	21	No. 14	10	No. 24	14	No. 34	10
No. 5	11	No. 15	22	No. 25	5	No. 35	11
No. 6	20	No. 16	19	No. 26	86	No. 36	23
No. 7	15	No. 17	21	No. 27	30	No. 37	15
No. 8	8	No. 18	13	No. 28	14	No. 38	40
No. 9	17	No. 19	39	No. 29	63	No. 39	41
No. 10	69	No. 20	12	No. 30	28	No. 40	17

Table 7. Tungsten in carbonate rocks

Description and locality	W (p.p.m.)
C 1 Sedimentary limestone, Dura River, Toro	0.2
C 2 Sedimentary limestone, Dura River, Toro	0.6
C 3 Sedimentary limestone, Hima River, Toro	0.4
C 4 Sedimentary limestone, Lake Kikorongo, Toro	0.7
C 5 Metamorphic limestone, Lake Kigezi	0.8
C 6 Marble, Rilnoi, Karamoja	0.8
C 7 Diopside marble, Lokitanyala, Karamoja	0.5
C 8 Calcite, Sukulu Hills, Mbale	0.5
C 9 Carbonatite, Sukulu Hills, Mbale	1.7
C 10 Carbonatite, Sukulu Hills, Mbale	1.9
C 11 Carbonatite, Tororo Rock, Mbale	0.6
C 12 Carbonatite, Busumbu, Mbale	8.3
C 13 Carbonatite, Lolekek, Karamoja	1.2
C 14 Carbonatite, Lokupoi, Napak, Karamoja	17.7

Basic and alkali-rich rocks

With one possible exception (DAVIES, 1953), basaltic rocks do not outcrop within the Protectorate and the basic-rock collection is limited to dolerites and amphibolites. Specimens of the potash-rich volcanic rocks from the south-west part of Uganda, described by HOLMES and HARWOOD (1937) have not been available, and determinations of tungsten in alkali-rich rocks have been limited to the sodium- and calcium-rich rocks described by DAVIES (1952, 1956) and KING (1948), and occurring only in the eastern part of the country.

From the results listed, it is apparent that both basic and alkali-rich rocks of the type examined contain greater quantities of tungsten than do most of the

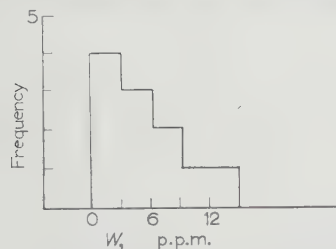


Fig. 2. Distribution of tungsten in dolerites and amphibolites. 3 p.p.m. interval.

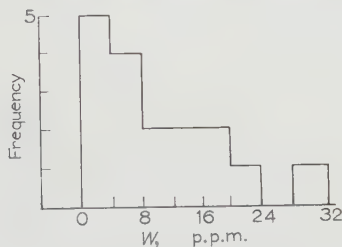


Fig. 3. Distribution of tungsten in Ca- and Na-rich alkali rocks. 4 p.p.m. interval.

granitic rocks examined. The frequency histograms of the results listed in Tables 3 and 4 are shown in Figs. 2 and 3. In both cases the distributions are positively skewed, but from the number of results available it is not possible to describe the distributions further.

For basic rocks, the arithmetic mean of the results listed is 5.2 p.p.m., the geometric mean 3.9 p.p.m., and the standard deviation λ , calculated on the assumption of lognormality, 0.36 (log). For the alkali-rich rocks examined the corresponding figures are arithmetic mean 10.0 p.p.m., geometric mean 5.7 p.p.m. and standard deviation λ , 0.43 (log).

Rocks of sedimentary origin (excluding carbonates)

As in the case of rocks of granitic composition, occasional high results appear to be typical of the Singo area, and occur in rocks of both the Singo Series and the Karagwe-Ankolean System. Frequency histograms of the results given in Table 5 are given in Figs. 4(a) and 4(b). As in the case of the rocks previously considered, the distribution is positively skewed. When the linear scale is replaced by a geometric one, as in Fig. 4(b), this positive skew disappears and the distribution approximates to lognormal. The lognormal distribution law suggested by AHRENS (1954) for igneous rocks is therefore also applicable to the distribution of tungsten in the sediments and metasediments of this composition group. The geometric mean of the results given is 3.6 p.p.m., the arithmetic mean 9.1 p.p.m., and the standard deviation λ , is 0.55 (log).

During 1957 an opportunity arose to examine the distribution of tungsten in a group of rocks of one specific metasedimentary type—the graphitic shales and

phyllites of the Karagwe-Ankolean System occurring at Ruhiza ferberite mine in south-west Uganda. The results obtained for the tungsten content of these samples are given in Table 6, and in the form of histograms in Figs. 5(a) and 5(b). The distribution again approximates to lognormal. The arithmetic mean is 23 p.p.m.,

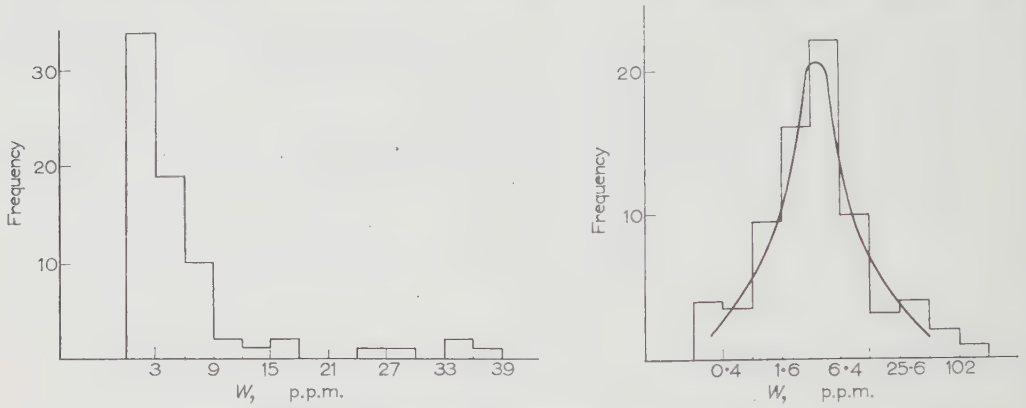


Fig. 4. Distribution of tungsten in sediments.
(a) 3 p.p.m. interval

(b) $\times 2$ interval.

the geometric mean 19 p.p.m., and the standard deviation 2. is 0.26 (log). The association of tungsten with rocks containing graphite has been established by these and other results, but where this association has been noted, tungsten mineralization has also been recorded. It is therefore not possible, on the basis of

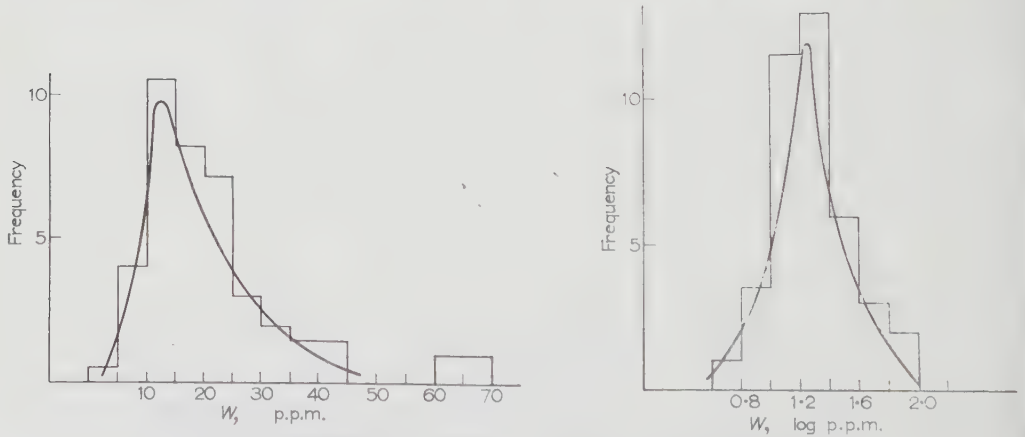


Fig. 5. Distribution of tungsten in graphitic shales and phyllites.

(a) 5 p.p.m. interval.

(b) log 0.2 p.p.m. interval.

the tungsten distribution alone, to decide whether the tungsten mineralization has given rise to rocks rich in this element, or whether rocks of high tungsten content have provided the material for the formation of the ore deposits.

Carbonate rocks

The Uganda Protectorate is composed largely of rocks of pre-Cambrian age. Very few carbonate rocks of this age are known, and in the Protectorate these are

limited to small outcrops of marbles in the Basement Complex System. A few small sedimentary limestone deposits of later age occur in river valley systems and small pockets of sedimentary and metamorphic limestones are found in association with the volcanic explosion craters in Western Uganda. Carbonatites occur in the Eastern Province in association with the alkali-rich rocks. Samples of carbonate rock from all these localities have been examined for tungsten, and the results are given in Table 7.

All the samples examined were found to contain less tungsten than the average content reported for arenaceous and argillaceous sediments, but this does not hold for the carbonatites examined. The variation of tungsten recorded in these specimens is somewhat similar to that observed in the associated silicate rocks (Table 4). The secondary limestone (calcite C 8) derived from the carbonatite contains only 0.5 p.p.m., a value comparable to the tungsten content of the sedimentary limestones.

Manganese minerals

Concentration of tungsten in manganese dioxide minerals of hypogene origin has been recorded by GOLDSCHMIDT (1954) from veins in a granite near Drammen in southern Norway. RANKAMA and SAHAMA (1949) have also recorded the presence of tungsten in manganese minerals—6300 p.p.m. in a specimen of hollandite and up to 7 per cent. in specimens of psilomelane. In view of this recorded association, a number of manganese minerals occurring in the Uganda Protectorate have been examined for tungsten (Table 8). The only concentration of this element recorded however was in the pyrolusite associated with the hypogene veins of the Singo area in which wolframite also occurs.

Iron and titanium minerals

A little tungsten appears to be concentrated in many of the iron and titanium minerals examined. Only in two samples of rutile was any concentration recorded. The samples were obtained from a pegmatite (T 10) containing also beryl, feldspar, tantalite and microlite, and from a quartz vein (T 11) of supposed hydrothermal origin. There is no evidence of tungsten mineralization at either of these localities.

Niobium and tantalum minerals

The association of tungsten with niobium and tantalum was recorded by SCHOELLER (1937) who reported between 0.02 and 2.02% WO_3 in ten analyses of earth-acid minerals, and by POLLETT (1957) who recently reported from 0.75 to 1.42% WO_3 in five specimens of columbite from Sierra Leone. The results of determinations of tungsten in some niobium and tantalum minerals from Uganda are given in Table 10. The first four specimens listed (N 1-4) were obtained from pegmatites, the fifth (N 5) by hand picking of the pyrochlore crystals from the residue remaining after solution of the carbonatite in hydrochloric acid.

Some rock-forming silicate minerals

The tungsten contents of some rock-forming silicate minerals are given in Table 11. In both the quartz and feldspar specimens examined very little tungsten

Table 8. Tungsten in manganese minerals

Description and locality	W (p.p.m.)
M 1 Pyrolusite, Karroo Beds, Buku, Entebbe, Mengo	4.0
M 2 Pyrolusite, Kaiso Beds, Kibuku, Toro	4.2
M 3 Pyrolusite, Karagwe-Ankolean Beds, Kigezi	12.2
M 4 Psilomelane, Mwirasando (tin) Mine, Ankole	4.6
M 5 Pyrolusite, Kilembe (copper-cobalt) Mine, Toro	3.0
M 6 Pyrolusite, old workings, Mugoye (tungsten) Mine, Singo	6200
M 7 Pyrolusite, new workings, Mugoye Mine, Singo	8000

was recorded. this is in agreement with the suggestion that tungsten does not readily replace silicon in silicate structures (for example see RINGWOOD, 1955). That the major part of the tungsten present in silicate rocks is contained in the accessory minerals is shown by the analysis of fractions obtained from the Entebbe granite (G 1 in Table 1). This total of 1.3 p.p.m. compares well with the analysis of the rock specimen, for which values of 1.4, 1.4 and 1.5 p.p.m. were obtained. The fractions were obtained from the crushed rock by bromoform separation and the use of a hand magnet.

Table 9. Tungsten in iron and titanium minerals

Description and locality	W (p.p.m.)
I 1 Magnetite, Sikusi, Mbale	3.1
I 2 Magnetite, Nangalwe, Mbale	2.7
I 3 Magnetite, Namekara, Mbale	14.5
I 4 Magnetite, Lolekek, Karamoja	20.4
I 5 Magnetite from granite, Entebbe	21.9
I 6 Micaceous haematite, Mengo	35.7
I 7 Haematite, Butale, Kigezi	6.8
I 8 Haematite, Ikamiro, Kigezi	8.8
I 9 Haematite, Kabale, Kigezi	9.3
I 10 Haematite, Mubulango, Kigezi	3.7
T 1 Perovskite, Sirumbusa, Mbale	26.4
T 2 Ilmenite, Namekara, Mbale	19.5
T 3 Ilmenite, Lolekek, Karamoja	12.0
T 4 Ilmenite, Kaabong, Karamoja	2.8
T 5 Ilmenite from beach, Entebbe	1.7
T 6 Ilmenite from mica-schist, Entebbe	5.2
T 7 Ilmenite from beach, Kyoga, Busoga	0.7
T 8 Ilmenite from pegmatite, Kigezi	56
T 9 Ilmenite from granite, Bulema, Kigezi	12.4
T 10 Rutile from pegmatite, Bulema, Kigezi	1500
T 11 Rutile, Kanyamasinga, Kayonza, Kigezi	2000
T 12 Rutile, Mwirasando, Ankole	74

Table 10. Tungsten in niobium and tantalum minerals

Description and locality	W (p.p.m.)
N 1 Columbite, Kabira Mine, Ankole	3200
N 2 Columbite-tantalite, Kihimbi Mine, Ankole	200
N 3 *Tantalite, Ruhuma Mine, Kigezi	93
N 4 Microlite, Bulema Mine, Kigezi	610
N 5 Pyrochlore, Lokupoi, Napak, Karamoja	44

* Specimen contains intergrowths of cassiterite.

The distribution patterns

In this paper the distribution of tungsten in the rocks of the Uganda Protectorate has been examined in some detail. In granitic and sedimentary rocks the distribution has been found to be positively skewed and to approximate to log-normal. In basic and alkali-rich rocks the number of observations is too small to enable the distribution to be accurately described as other than positively skewed. Predictions based upon assumptions of lognormality should not however be seriously in error: thus for example, calculation of the limits for 95 per cent of the total number of observations will not result in the prediction of negative concentrations as would be the case if normality were assumed.

Difficulties in describing exact distributions in geological materials have already been outlined (AHRENS, 1957) and must be taken into account in considering the applicability of his geochemical law (AHRENS, 1954) to the distribution of tungsten. Thus in all the rock types examined the number of observations made has been too small to enable rigorous statistical treatment to be applied. Moreover in the case of the granitic rocks (Table 1), the specimens cannot be considered to be a true "single population", but rather constitute a number of specific types ranging from granitic gneiss to magmatic granite. The regional bias suggests that no simple overall pattern is followed by the distribution of tungsten in these rocks, and that the conclusion as to the lognormal nature of the distribution can only be approximately true.

Table 11. Tungsten in some silicate minerals

Description and locality	W (p.p.m.)
Quartz from granite, Entebbe, Mengo	0.1
Felspar from granite, Kateti Ridge, Ankole	0.1
Muscovite from mica-schist, Entebbe, Mengo	0.4
Green biotite from carbonatite, Sukulu Hills, Mbale	2.8
Biotite from biotite-gneiss, Kaabong, Karamoja	6.0
Phlogopite from carbonatite, Bukusu, Mbale	22.5
Tourmaline from tourmaline-rock, Sango Bay, Masaka (Bukoban Series)	15.4

Table 12

Fraction	Approx. % of fraction in rock	W (p.p.m. in fraction)	W contributed to rock (p.p.m.)
Quartz-felspar	95	0.2	0.2
Magnetite	3	21.9	0.7
Ilmenite (+ a little magnetite)	1	24.0	0.2
Zircon, biotite, garnet and other heavy minerals	1	17.5	0.2
		total	1.3

A similar conclusion can be reached in the case of the sedimentary rocks, where the later rocks contain more tungsten than the earlier ones (see below). The closest approach to lognormality was recorded in the case of the distribution of tungsten in the graphitic phyllites from Ruhiza mine, where the samples had all been taken from a specific metasedimentary rock.

SUMMARY OF ABUNDANCE DATA

The following table has been compiled from values reported in the literature for the tungsten content of rock and composite rock samples.

Sample	W (p.p.m.)
Granite, Schwarzwald, Germany (HH)	83
Composite of 282 igneous rocks, central Europe (HH)	69
Composite of 67 gabbros and norites, central Europe (HH)	24
Granite, Harz, Germany (NN)	4
Granite, Norway (NN)	30
Granite, Andes (NN)	20
Basalt, Kaiserstuhl (NN)	20
Basalt, Sweden (NN)	5
Basaltic lava, Vesuvius (NN)	20
Kimberlite (NN)	3
Acidic rocks, Central Roslagen, Sweden (L)	7
Basic rocks, Central Roslagen, Sweden (L)	10
Composite samples of granitic and intermediate rocks mainly from N. America, but including one composite from Africa (S), 11 values from 1 to 2 p.p.m., average	1.5
Schist, Australia (WF)	1-2

(HH: HEVESY and HOBIE (1933), NN: I. and W. NODDACK (1931), L: LUNDEGARDH (1946), S: SANDELL (1946), WF: WILSON and FIELDS (1944))

The oft-quoted figure of 69 p.p.m. for igneous rocks given by HEVESY and HOBIE (1933) is clearly in error, and much of the data of NODDACK and NODDACK

(1931) and LUNDEGÅRDH (1946) should also be rejected or revised in the light of the results given by SANDELL and those published here.

The average or arithmetic mean of the results given here for the tungsten content of granitic rocks is 2.1 p.p.m., but this figure is misleading, including as it does results from rocks of the mineralized area of Singo, which are clearly not typical specimens. By excluding these results, an average of 1.4 p.p.m. is obtained, which is considered to be a better abundance value for rocks of granitic composition. KURODA and SANDELL (1954) have observed that the granites from the African continent tend to be poor in molybdenum, and the possibility exists that these rocks may likewise show regional variation of tungsten on the same continental scale. Nevertheless the figure of 1.4 p.p.m. is in good agreement with the results of SANDELL (1946) for composite samples mainly from North America, obtained by a completely different method. On these grounds, and also because the typical rocks of Uganda extend far beyond the frontiers of the Protectorate, this value of 1.4 p.p.m., based upon 52 samples can be recommended for the terrestrial abundance of tungsten.

The abundance values obtained for carbonate, basic and alkali-rich rocks are based upon very small numbers of determinations, and can therefore be regarded only as magnitudes until further work is done.

The average value for the tungsten content of the sedimentary rocks examined is 9.1 p.p.m., but this value cannot represent a true abundance figure as rocks from the mineralized areas of Singo and Kigezi have been included. If the samples from these areas are excluded, the average tungsten content of the remaining sediments and metasediments is 3.9 p.p.m. This value compares reasonably well with the only other recorded value for the tungsten content of such rocks—1 to 2 p.p.m., given by WILSON and FIELDS (1944) for an Australian schist. As with granitic rocks, regional variation of tungsten content has been recorded, and this is correlated with the age of the systems (see below), and for this reason further work is required before this abundance value can be considered to be of general application. The following table gives a summary of the abundance data presented here.

Sample	W (p.p.m.)
Granitic rocks (52 samples)	1.4
Dolerites & amphibolites (11 samples)	5.2
Na- and Ca-rich alkali rocks (17 samples)	10.0
Sediments and metasediments (60 samples)	3.9
Graphitic phyllites from Ruhiza (40 samples)	23
Limestones (7 samples)	0.6
Carbonatites (6 samples)	5.2

ASPECTS OF THE GEOCHEMISTRY OF TUNGSTEN

Sedimentary rocks

Although the number of determinations of tungsten in the sedimentary rocks of the Uganda Protectorate is insufficient to enable accurate computations of

averages to be made for each system, the results obtained (Table 13) do illustrate a distinct trend towards higher average tungsten contents in the younger rocks. In the table the systems are listed in order of increasing age.

In dealing with rocks of granitic composition a regional bias was noted. It is probable that this bias arises from the same cause as that shown above in the sedimentary rock systems since the proportion of "younger" granitic rocks in the regional groups increases in the order in which the average tungsten content increases.

Table 13

System	No. of samples	g.m. (p.p.m.)
Kaiso-Kisegi Beds	8	5.3
Karoo Beds	4	4.5
Bukoban Series	1	5.5
Bunyoro Series	5	1.7
Karagwe-Ankolean System	19*	4.8
Samia Series	3	2.6
Bulugwe Series	3	1.1
Toro System	9	1.2
Basement Complex System	8	0.6

* Rocks from the mineralized areas of Singo and Kigezi omitted.

This variation of tungsten content with age is in general accord with the suggestion of SULLIVAN (1948), who explains the existence of ore deposits of tungsten (amongst other metals) on the basis of the introduction, in this case, of tungsten with basic rocks by "volcanic activity", followed by cycles of erosion and granite formation. This is possible since it has been shown that dolerites and amphibolites contain more tungsten than granitic rocks, and, although no basaltic rocks have been available for examination, it is probably justifiable to assume that they too contain more tungsten than granitic rocks.

Much of the Uganda Protectorate is covered with pre-Cambrian sediments and metasediments and the source material of these rocks is rather uncertain. The rocks of the Karagwe-Ankolean System for example were laid down in a geosyncline which extends far beyond the limits of the Protectorate, and the materials from which these rocks were derived may have travelled great distances. The relative paucity of basic-rock types within the Protectorate at the present time is therefore no criterion of the contribution of basic rock material to these older sediments.

In the case of the Kaiso-Kisegi Beds of Plio-Pleistocene age, however, it is known that the material comprising these beds is fairly local in origin. BISHOP (private communication) has suggested that a large contribution to the material of these beds was from the alkali-rich volcanics of the Eastern Province. Studies of the Katonga and Kafu drainage systems have shown that in Plio-Pleistocene times the main drainage of the Protectorate was from east to west, and it is probable that much of the vast amount of material known to have been eroded

from the volcanoes of the Eastern Province travelled via the Kafu River to the Western Rift Valley where the Kaiso-Kisegi Beds were being deposited.

The surviving rocks of the alkali-rich volcanoes are (as shown in Table 4) comparatively rich in tungsten, the average of the results listed is 10.0 p.p.m., as compared with 1.4 p.p.m. for rocks of granitic composition. Thus a large scale contribution of material from the alkali rocks will give rise to a sediment containing an increased proportion of tungsten if, as seems probable, the tungsten of the original rock is largely retained chemically or mechanically in the residual sediment.

Although it is known that tungsten is not carried far in solution (for example RANKAMA and SAHAMA (1949) have suggested that in the presence of calcium in solution, scheelite would be precipitated), it is not known at what stage in the erosion cycle the major part of the tungsten enters into solution prior to deposition. If chemical breakdown of the rock forming minerals and the deposition of the tungsten is not accompanied by the deposition *in toto* of the arenaceous and argillaceous material from which the tungsten has been derived then the fine grained later sediments will contain less tungsten than the earlier sediments. The quantities released and the amount of scheelite formed is so small that the settling rate of the tungsten would be governed by the nature of the adsorbants present in solution—such as manganese or ferric hydroxides. The presence of a suitable adsorbent may well give rise to local concentrations of tungsten within the residual sediment. This may provide an explanation of the recorded association of tungsten with graphite in the graphitic phyllites of the Karagwe-Ankolean System in Kigezi, the tungsten having been adsorbed by organic matter present in the basin of deposition.

Granitic rocks

That tungsten is not associated with quartz and felspar in granitic rocks, but appears predominantly in the accessory minerals has been demonstrated in Tables 11 and 12. RINGWOOD (1955) suggests that in a silicate magma the tungsten is present as the complex ion WO_4^{2-} and that as a result of the charge difference between this complex and the complex ion SiO_4^{4-} , tungstate ions are not readily accepted into silicate structures and therefore accumulate in the residual magma. Appreciable quantities of tungsten may be removed from the magma by the crystallization of accessory minerals, otherwise the concentration of this element will rise until primary minerals of tungsten can crystallize.

The same charge difference of two which exists between the complexes WO_4^{2-} and SiO_4^{4-} also exists between the tungsten complex and the titanium complex TiO_4^{4-} , for which the tungstate complex substitutes to a considerable extent. The controlling factor is therefore probably not the charge difference, but the difference in size of the central atom of the complex, tungsten W^{6+} , $r = 0.62 \text{ \AA}$, substituting with relative ease for titanium, Ti^{4+} , $r = 0.68 \text{ \AA}$, but only with difficulty for silicon, Si^{4+} , $r = 0.42 \text{ \AA}$ (ionic radii, AHRENS, 1952). An alternative explanation may be that tungsten is present in the quadrivalent state, W^{4+} , $r = 0.70 \text{ \AA}$, substituting for titanium Ti^{4+} , $r = 0.68 \text{ \AA}$ (and also for zirconium Zr^{4+} , $r = 0.79 \text{ \AA}$), atoms with similar charges and comparable ionic radii.

The appearance of primary minerals of tungsten is characteristic of the late

hypothermal stage of granite emplacement, and wolframite ores of this type are known to occur in both the Singo and Kigezi areas of Uganda. Because of the smaller size of the ferrous ion Fe^{2+} , $r = 0.74 \text{ \AA}$, as compared with that of manganese Mn^{2+} , $r = 0.80 \text{ \AA}$, iron will be preferentially incorporated into the iron-manganese tungstates and manganese will be concentrated in the residual solutions and appear to an increasing extent in the later crystalates. This well known effect is illustrated in the case of wolframite ores from Uganda in the following table, where manganese determinations are reported in a number of samples from three hypothermal veins.

Table 14. MnO (%)

	Kyasampawo Singo	Bahati Kigezi	Nyhang'a Kigezi
increasing ↓ depth	4.78	4.97	5.08
	4.50	4.02	4.99
	4.08	3.21	4.08
	3.79	2.92	3.68

Analysts: B. C. KING, H. M. S. and P. G. J.

The earlier iron-manganese tungstates occurring at depth contain a higher proportion of iron and lower proportion of manganese than the later tungstates occurring at the higher levels of the veins. Syngenetic iron-manganese tungstate (ferberite) also occurs in the Kigezi District (PARGETER, 1956) associated with the graphitic phyllites of the Karagwe-Aukolean System. Unlike the epigenetic tungsten ores, these tungstates show little or no variation in manganese content with depth.

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REFERENCES

- AHRENS L. H. (1952) *Geochim. Cosmochim. Acta* **2**, 168.
 AHRENS L. H. (1954) *Geochim. Cosmochim. Acta* **5**, 49.
 AHRENS L. H. (1957) *Geochim. Cosmochim. Acta* **11**, 205.
 ALLEN S. H. and HAMILTON M. B. (1952) *Anal. Chim. Acta* **7**, 483.
 DAVIES K. A. (1952) Memoir No. VII. Geological Survey Dept., Entebbe, Uganda.
 DAVIES K. A. (1953) *Geol. Mag.* **90**, No. 4, 268.
 DAVIES K. A. (1954) Memoir No. VIII. Geological Survey Dept., Entebbe, Uganda.
 DUROVIC S. (1958) *Geochim. Cosmochim. Acta* **15**, 330-336.
 GOLDSCHMIDT V. M. (1954) *Geochemistry* (Edited by MUIR A.). Oxford University Press.
 HEVESY VON G. and HOBBIIE R. (1933) *Z. anorg. Chim.* **212**, 134.
 HOLMES A. and HARWOOD H. F. (1937) Memoir No. III, Part II. Geological Survey Dept., Entebbe, Uganda.

- JEFFERY P. G. (1956) *Analyst* **81**, 104.
- JEFFERY P. G. (1957) *Analyst* **82**, 558.
- KING B. C. (1948) Memoir No. V. Geological Survey Dept., Entebbe, Uganda.
- KURODA P. K. and SANDELL E. B. (1954) *Geochim. Cosmochim. Acta* **6**, 35.
- LUNDEGÅRDH P. H. (1946) *Ark. Kemi Min. Geol. A* **23**, No. 9.
- NODDACK I. and NODDACK W. (1931) *Z. phys. Chem. A* **154**, 207.
- PARGETER R. C. (1956) *Records of Geological Survey for 1954*. Geological Survey Dept., Entebbe, Uganda.
- POLLETT J. D. (1957) *Annual Report, Geological Survey Dept. for 1955*. Geological Survey Dept., Freetown, Sierra Leone.
- RANKAMA K. and SAHAMA T. G. (1949) *Geochemistry*. University of Chicago Press.
- RINGWOOD A. E. (1955) *Geochim. Cosmochim. Acta* **7**, 242.
- SANDELL E. B. (1946) *Amer. J. Sci.* **244**, 643.
- SCHOELLER W. R. (1937) *The Analytical Chemistry of Niobium and Tantalum*. Chapman and Hall, London.
- SULLIVAN C. J. (1948) *Econ. Geol.* **43**, 471.
- WILSON S. H. and FIELDÉS M. (1944) *Analyst* **69**, 12.

New occurrences of ferroselite (FeSe_2)*

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Abstract—Iron selenide from the uranium–vanadium ores of the Colorado Plateau was under investigation when ferroselite was described as a new mineral in Russia by BUR'YANOVA and KOMKOV (1955). Association of ferroselite with selenian pyrite and marcasite within discrete areas of these uranium–vanadium deposits suggests an unusual environment of formation. Its association with apparent low temperature assemblages in the United States and Russia indicates that its minimum temperature of formation is quite low. Chemical analyses of ferroselite agree well with the theoretical formula FeSe_2 ; material from the Virgin no. 3 mine, Montrose County, Colorado, gives the formula $\text{FeSe}_{2.07}$ and that from the A.E.C. no. 8 mine, Temple Mountain, Utah, gives the formula $(\text{Fe}, \text{Co})\text{Se}_{2.08}$. The similarity of hastite and ferroselite suggests that a complete series FeSe_2 – CoSe_2 may exist. In contrast to this, pyrite associated with ferroselite apparently will camouflage only 4 per cent (molecular) FeSe_2 within its structure. Ferroselite cannot be distinguished from rammelsbergite (FeAs_2) by X-ray or in polished section; therefore, the exact identification of these two minerals can be made only by specific tests for As or Se. As hastite (CoSe_2) and marcasite are in the same structure group as ferroselite and rammelsbergite, identification of these minerals should include qualitative chemical determinations.

INTRODUCTION

FERROSELITE was identified during an investigation of selenium-bearing iron sulphides associated with sedimentary-type uranium deposits in the Western United States (COLEMAN and DELEVAUX, 1957). This mineral was found in several iron sulphide concentrates showing abnormal selenium content. These same concentrates when examined closely revealed the presence of material whose X-ray pattern was similar to rammelsbergite.

BUR'YANOVA and KOMKOV (1955) pointed out the similarity of ferroselite and rammelsbergite. The verification of ferroselite in the iron sulphide selenide concentrates from Temple Mountain, Utah, was not established until a complete chemical analysis had been made, as it was not possible to distinguish ferroselite (FeSe_2), hastite (CoSe_2), or rammelsbergite (FeAs_2) by X-ray techniques. The work of KULLERUD and DONNAY (1958) on this same material clearly shows the striking similarity of ferroselite and rammelsbergite.

Following the identification of ferroselite from the Temple Mountain deposits, the studies of WEEKS *et al.* (1957) and COLEMAN and DELEVAUX (1957) on the Colorado Plateau uranium vanadium deposits have shown ferroselite to be commonly present in the Uruan and Temple Mountain mining districts.

OCCURRENCE

Ferroselite, in the original description by BUR'YANOVA and KOMKOV (1955) and BUR'YANOVA (1956), is reported to occur in Middle Devonian sandstones of the Tuvinsk Tuva Autonomous Territory, U.S.S.R. In their description, BUR'YANOVA and KOMKOV show that ferroselite forms within calcite–laumontite cemented psammitic quartz sandstones. These sandstones contain volcanic ash

* Publication authorized by the Director, U.S. Geological Survey.

and effusive rock fragments derived from Paleozoic volcanism. Barite, pyrite, sphalerite and chalcopyrite are associated with ferroselite in these Middle Devonian sedimentary rocks.

In a later paper, BUR'YANOVA and others (1957) describe cadmoselite (CdSe) as a new mineral associated with ferroselite, presumably from the same locality; and from this occurrence they list clauthalite, cadmian sphalerite, native amorphous selenium and pyrite as accompanying minerals. No mention is made of associated ore deposits within the sediments and one would assume that the ferroselite formed during diagenesis of the sediments. They suggest that the selenium was derived from the attendant Paleozoic volcanic activity during the time of deposition, and from this dispersed source the selenium was enriched to form these selenides. In a general way the Russian occurrence is quite similar to the Colorado Plateau ferroselite occurrences where the source of the selenium has been related to volcanic activity (COLEMAN and DELEVAUX, 1957).

Ferroselite was found in three different types of uranium-vanadium ores from the Colorado Plateau. It was first identified in the "asphaltite" ores from the A.E.C. no. 8 mine, Temple Mountain, San Rafael District, Emery County, Utah. Here the ore is concentrated in coarse sandstone and conglomerates (Chinle formation of Triassic age) impregnated with carbonaceous material and containing coalified wood (KELLY and KERR, 1958). Ferroselite is usually peripheral to the iron sulphide concentrations and uranium ore, forming prismatic crystals in the intergranular voids of the sandstone where they are neither intergrown with nor do they replace the associated iron sulphides. Ferroselite cannot readily be distinguished in the field from pyrite or marcasite as the individual grains rarely exceed 1 mm, and its colour is quite similar to that of the iron sulphides. Pyrite associated with ferroselite in the A.E.C. no. 8 mine contains 0.50 per cent (w/w) selenium and up to 1 per cent (w/w) cobalt. The oxidation of ferroselite and associated sulphides in this mine produces a characteristic rose-red bloom which has been identified as cobaltomenite, $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$ (oral communication, MROSE and HOUSTON, U.S. Geological Survey). This distinct oxidation product serves as a field guide to the general distribution of ferroselite on the mine walls.

Following the identification of ferroselite in the Temple Mountain Area, the mineral was found to be rather common in the Virgin no. 3 mine, Uravan District, Montrose County, Colorado, in collections made by SHAW, U.S. Geological Survey. More recently a detailed mineralogical study of this district by WEEKS *et al.* (1957) has shown that ferroselite is a rather common mineral in the ores from the Salt Wash member, Morrison formation of Jurassic age. In the Long Park-Club Mesa area, ferroselite has been identified in the ores from the Bitter Creek, Vanadium King no. 6, Firecracker no. 1, Long Park no. 12, Barkley, and Triangulation mines, and oxidized remnants have been observed at the LaSalle mine (written communication, WEEKS, U.S. Geological Survey).

Within the Uravan district, ferroselite occurs as thin zones bordering the vanadiferous uranium ore bodies within sandstone lenses and also as discontinuous stringers associated with coalified wood within the ore. Here ferroselite crystallizes in the intergranular voids of the host sandstone producing discrete individual crystals. The crystal habit of ferroselite from this district is characterized by cruciform

penetration twins along with the single prismatic crystals. Oxidation of the ferroselite in this area produces a pinkish crust of monoclinic native selenium rather than cobaltomenite as in the A.E.C. no. 8 mine.

Ferroselite has also been identified in the Gray Sill mine, Rico district, Colorado. Here the ferroselite forms thin bands along the boundary of the vanadium ore similar to the galena-clausthalite bands described from the Rifle mine, Colorado (COLEMAN and DELEVAUX, 1957, p. 506). The ferroselite is the only sulphide-selenide mineral present within these bands forming discrete crystals intergranular to the detrital grains of the Entrada sandstone of Jurassic age.

ENVIRONMENT OF DEPOSITION

Ferroselite usually crystallizes in discrete bands or zones peripheral to ore in the Colorado Plateau uranium-vanadium deposits suggesting that it may form under a limited range of conditions in this particular environment. The lack of replacement or intimate contact with sulphides also indicates that the FeSe_2 may form in unusual chemical environment or as a result of distinct periods of mineralization.

A recent study of sulphides associated with the uranium-vanadium deposits (COLEMAN and DELEVAUX, 1957) has shown that selenium becomes highly concentrated in certain deposits. In these seleniferous deposits, free selenides such as clausthalite (PbSe), ferroselite, and rarely eucairite ($\text{Cu}_2\text{Se} \cdot \text{Ag}_2\text{Se}$) may be present; however, in most instances free selenides are lacking and the selenium is camouflaged in the sulphide minerals. Generally, pyrite, marcasite and galena are the most abundant sulphides present, and in these minerals selenium is commonly found substituting for sulphur. Ferroselite is associated with pyrite and marcasite in these ores; but apparently it forms only when the selenium supply at the time of crystallization exceeds the amount which can be camouflaged in the associated sulphides.

Ferroselite is not in intimate contact with galena in any of the deposits, but where selenium-bearing ores contain galena, most of the selenium is contained within this mineral and the associated iron sulphides contain only minor amounts of selenium. Analysis of the selenian galenas from these deposits reveals that a continuous variation between galena and clausthalite exists in the Colorado Plateau deposits (COLEMAN, in press).

COMPOSITION OF NATURAL FeSe_2

The works of BUR'YANOVA and KOMKOV (1955) and BUR'YANOVA (1956) on ferroselite, and RAMDOHR and SCHMITT (1955) on hastite has shown that these two minerals are isostructural. The close similarity in the X-ray patterns of ferroselite, hastite and rammelsbergite makes it difficult to establish their identity without chemical analyses. The presence of cobalt in the iron selenide from the A.E.C. no. 8 mine detected by preliminary spectrographic analyses suggested that it might be hastite admixed with pyrite; however, it was not possible to establish the exact identification until a complete chemical analysis had been made (Table 1).

The analysis, when calculated to fit the formula FeSe_2 , showed that 4.2 per cent of the total iron had been replaced by cobalt; thus the material from the

Table 1. Analyses of ferroselite and selenian pyrite

Sample no.	1	2	3	4	5	
<i>Chemical analyses in weight per cent*</i>						
Fe	23.8	25.2	25.9	26.13	43.68	
Co	1.1	—	—	—	—	
As	—	—	—	—	4.24	
S	—	—	—	—	50.31	
Se	73.2	73.8	73.6	73.87	1.42	
	98.1	99.0	99.5	100.00	99.65	
Calculated formulae	(Fe, Co)Se _{2.08}	FeSe _{2.07}	FeSe _{2.01}	FeSe _{2.00}	(Fe, As) (S, Se) _{1.9}	
<i>Spectrographic analyses in weight per cent†</i>						
>10	Fe	Major Fe			>10	Fe
1-5	Co Si	0.1 Si			1-5	As
0.1-0.5	Al Ni	0.01 B Zr			0.01-0.05	Al Ni Si
0.05-0.1	Ti Ca	0.003 Mg Co Cu	—	—		Mo Mn Zr
0.01-0.05	Pb Mn Mg	Ni Pb				Nd La
	V B Cu	0.0003 Ag			0.005-0.01	Co Sn Pb
0.005-0.01	Nb Sr					Y
0.001-0.005	Ba Zr Sn				0.001-0.005	Mg Ba Cu
0.0005-0.001	Cr				0.0005-0.001	Cr
0.0001-0.0005	Ag					

(1) Cobaltian ferroselite, A.E.C. no. 8 mine, Temple Mt., Utah (121-RGC-55).

(2) Ferroselite, Virgin no. 3 mine, Montrose County, Colorado (S-1), collected by D. R. SHAW, U.S. Geological Survey.

(3) Synthetic ferroselite, synthesized by G. KULLERUD, Geophysical Laboratory, Carnegie Institution of Washington.

(4) Theoretical ferroselite.

(5) Selenian pyrite, Vitro mine, Fremont County, Wyoming (AW-218-54).

* Chemical analyses (1), (2) and (3) made by A. M. SHERWOOD; analysis (5) made by H. LEVINE, U.S. Geological Survey.

† Semiquantitative spectrographic analyses made by K. V. HAZEL and J. HAFFTY, U.S. Geological Survey.

A.E.C. no. 8 mine can best be called cobaltian ferroselite. Analysis of the ferroselite from the Virgin no. 3 mine, Uravan district, reveals that its composition is similar to that given for theoretical FeSe_2 (Table 1). Synthetic ferroselite made by KULLERUD (Geophysical Laboratory, Carnegie Institution of Washington) was kindly supplied to the author for analysis and the results are given in the same table for comparison. The d -spacings of the cobaltian ferroselite from A.E.C. no. 8 mine, ferroselite from Virgin no. 3 mine and synthetic ferroselite are the same. Details on the structure of ferroselite are given by KULLERUD and DONNAY (1958). The calculated formulae for these three analyses agree quite well with the theoretical (Table 1); however, they all show a slight deficiency in iron indicating that elements other than cobalt may be substituting for iron or possibly some of the iron positions in the structure may be vacant. The presence of other elements is confirmed by spectrographic analyses, but it is not known if these elements substitute for iron (Table 1). The calculated formula for $\text{FeSe}_{2.01}$ from the analysis made on synthetic ferroselite is very close to theoretical $\text{FeSe}_{2.00}$ and within the limits of accuracy for these analytical determinations. The analysis of ferroselite given by BUR'YANOVA (1956) shows 26.43 per cent (w/w) Fe, 68.42 per cent (w/w)

Se. and residue 4 per cent (w/w): Te and S were not detected. Calculating the formula for ferroselite from the analysis given for the Tuva material produces $\text{FeSe}_{1.83}$ which diverges considerably from the ideal formula. Considering that a 4 per cent residue is reported along with a considerable excess of iron, the material used for analysis must have been impure.

The structural similarity of ferroselite and hastite coupled with the fact that 1.1 per cent (w/w) cobalt was found in the material from the A.E.C. no. 8 mine would seem to indicate that a complete solid solution between FeSe_2 - CoSe_2 is possible. The unit cell dimensions obtained by KULLERUD and DONNAY (1958) on the cobaltian ferroselite are quite similar to those found by BUR'YANOVA and KOMKOV and the synthetic ferroselite of KULLERUD. Thus the diadochic substitution of cobalt for iron seems to have little effect on the structure.

The selenian pyrites found within the uranium-vanadium deposits contain selenium in limited amounts. The maximum FeSe_2 thus far reported in pyrite is about 4 per cent (molecular) (COLEMAN and DELEVAUX, 1957). An analysed selenian pyrite from the uranium ores of the Vitro mine, Fremont County, Wyoming, shows 1.42 per cent (w/w) Se (Table 1). This pyrite has a unit cell ($a = 5.43 \pm 0.01 \text{ \AA}$) somewhat greater than the value given for pyrite ($a = 5.41 \text{ \AA}$) by GORDON (1951) and LEPP (1956). The substitution of selenium for sulphur in the pyrite structure may produce an expansion of the unit cell similar to that demonstrated in the galena-clausthalite series (COLEMAN, in press); however, 4.24 per cent (w/w) of As reported in this analysis may also account for this expansion of the unit cell. Further experimental work is needed to determine the upper limits of solid solution of FeSe_2 in FeS_2 and its effect on the pyrite structure. Extensive solid solution between pyrite and ferroselite seems to be a rather remote possibility even at high temperatures and pressures, since pyrite is cubic and ferroselite is orthorhombic. In contrast, the maximum FeSe_2 reported in marcasite, the orthorhombic dimorph of FeS_2 , is 0.63 per cent (molecular) (COLEMAN and DELEVAUX, 1957).

SUMMARY

The recent description of ferroselite from Russia and its occurrence in the Colorado Plateau uranium-vanadium deposits would suggest that it is not an uncommon mineral. Because of its similarity to marcasite, rammelsbergite and hastite, the exact identification of ferroselite can only be established by a combination of X-ray and chemical analysis.

The observations on ferroselite's natural environment of deposition indicate that it probably forms at low temperatures; however, its stability as shown from the experimental work of KULLERUD and DONNAY (1958) is well within the P - T conditions found in hydrothermal deposits. Ferroselite may very well be present in some seleniferous ore deposits where it has been misidentified for its more common isotypes.

Acknowledgements—The author is grateful for the interest taken by G. KULLERUD and G. DONNAY in the problem of synthesis and crystal structure of ferroselite: their work is presented in *Geochim. Acta* **15**, pp. 73–79. I am indebted to D. R. ROSS, I. ADLER and K. V. HAZEL, of the U.S. Geological Survey, for their preliminary X-ray and spectrographic work which led to

the discovery of this new occurrence of ferroselite. Information regarding occurrences was kindly furnished by A. D. WEEKS and A. H. TRUESDELL, U.S. Geological Survey. Mr. TRUESDELL was also helpful in the difficult task of purifying the iron selenide for analysis. Translations of the Russian papers on ferroselite and cadmoselite were made by M. FLEISCHER, U.S. Geological Survey. This investigation was conducted by the U.S. Geological Survey on behalf of the Division of Raw Materials of the U.S. Atomic Energy Commission.

REFERENCES

- BUR'YANOVA E. Z. and KOMKOV A. I. (1955) Ferroselite—a new mineral. *Dokl. Akad. Nauk SSSR*, **105**, 812–813; (1956) *Chem. Abs.* **50**, 9239.
- BUR'YANOVA E. Z. (1956) Ferroselite. *Zap. Vses. Mineral. Obshch.* **85**, 286–291; (1957) *Chem. Abs.* **51**, 2477.
- BUR'YANOVA E. Z., KOVALEV G. A. and KOMKOV A. I. (1957) The new mineral cadmoselite. *Zap. Vses. Mineral. Obshch.* **86**, 626–628.
- COLEMAN R. G. and DELEVAUX M. (1957) Occurrence of selenium in sulphides from some sedimentary rocks of the Western United States. *Econ. Geol.* **52**, 499–527.
- COLEMAN R. G. (1959) Natural occurrence of galena–clausthalite solid-solution series. *Amer. Min.* **44**, (In press).
- GORDON R. B. (1951) Some measurements on minerals of the pyrite group. *Amer. Min.* **36**, 918–920.
- KELLEY D. R. and KERR P. F. (1958) Urano-organic ore at Temple Mountain, Utah. *Bull. Geol. Soc. Amer.* **69**, 701–756.
- KULLERUD G. and DONNAY G. (1958) Natural and synthetic ferroselite. *Geochim. et Cosmochim. Acta.* **15**, 73–79.
- LEPP H. (1956) Precision measurements of the cell edge of synthetic Pyrite. *Amer. Min.* **41**, 347–348.
- RAMDOHR P. and SCHMITT M. (1955) Vier neue natürlliche Kobaltselenide vom Steinbruch Trogtal bei Lauthenthal im Harz. *Neues Jb. Miner. Mh.* **6**, 133–142.
- WEEKS A. D., TRUESDELL A. H. and HAFFTY J. (1957) Nature of the ore boundary and its relation to diagenesis and mineralization, Uravan District, Colorado (abs.) *Bull. Geol. Soc. Amer.* **68**, 1810.

LETTERS TO THE EDITOR

An upper limit for radiogenic A^{38} in potassium minerals

GERLING, LEVSKII and AFANAS'YEVA (1956) detected what they believed to be small mounts of A^{38} in potassium-containing minerals (mica, lepidolite, sylvite). They assumed that the A^{38} was produced by the decay of a long-lived isomer of K^{38} having a decay constant of $9 \times 10^{-10} \text{ yr}^{-1}$ and an atomic abundance of 10^{-10} in potassium. WASSERBURG and LIPSON (1958) attempted to substantiate this report but were unable to obtain a definitive answer inasmuch as residual A^{38} in their mass spectrometer from earlier measurements resulted in a background. In a later investigation, WASSERBURG and BIERI (1958) showed for two potassium minerals that if A^{38} existed, it had an abundance of an order of magnitude less than would be predicted from the K^{38} abundance and decay constant given by GERLING *et al.*

We have investigated the A^{40}/A^{38} ratio in two feldspars of known age. Samples of approximately 2 g were placed in a crucible heated by radiation and mounted in a vacuum chamber which is part of a gas manifold attached to a mass spectrometer. The chamber is separated from the mass spectrometer tube by a valve. This direct connexion between the gas extraction system and the spectrometer tube permits a sensitive test of the vacuum tightness of the apparatus and makes possible an analysis of the sample immediately after the extraction. Heating the crucible to a temperature of 1900°C for 30 min resulted in a release of at least 70 per cent of the argon. During the heating process and for an additional 15 min, the gas was purified by titanium sponge heated to $600^\circ\text{--}700^\circ\text{C}$ in an appendage to the vacuum chamber. Immediately after the extraction and purification process a small fraction (approximately 1/1000, i.e. $5 \times 10^{-6} \text{ cm}^3$) of the gas was admitted to the all-metal Nier-type 60° single-focusing mass spectrometer tube. Prior to the admission of the gas, the mass spectrometer tube was isolated from its pumping system so that the analyses could be made under static conditions. Before and after the analyses of the samples, blank runs were made. In these, small peaks were observed in the region from mass 36 to 44. These peaks are attributed to traces of hydrocarbon impurities. The spectral pattern was reproducible in different runs. In particular, the residual 38 peak lay in the range of from 20 to 50 per cent of the total 38 peak associated with the sample.

A continuous observation of the spectrum after the admission of the sample showed the A^{40} to decrease slowly with time. This is due in part to adsorption of argon on the clean walls of the mass spectrometer tube and to "pumping" caused by the ionization of the gas. On the other hand, the 36 and 38 peaks grew slowly with time, showing that some process or processes contributed to these peaks at a greater rate than the adsorption and pumping action present. The 38 peak grew faster than the 36. In blank runs the growth rates were much smaller than when a sample was present. Experiments showed that the growth was due primarily to the release of previously adsorbed argon from the spectrometer tube. This phenomenon was observed in spite of the very extensive heating (in total more than 100 hr at 300°C) of the entire vacuum system prior to this investigation. A more complete discussion of measurement procedures will appear elsewhere.

Table 1 shows values for the limits of the ratios of the three peaks when the peaks were extrapolated back to the time of admission of the gas to the mass spectrometer tube. The ratio $A^{40}/(36 \text{ peak})$ indicates that the contamination of the radiogenic argon with air argon was small. As in the WASSERBURG and BIERI work, contribution to the 38 peak from hydrocarbons and from air argon introduced with the sample gas is so small that even the uncorrected ratio $A^{40}/(38 \text{ peak})$ is larger than the A^{40}/A^{38} ratio predicted from the constants given by GERLING *et al.* When correction was made for the residual hydrocarbons and air present, lower limits of

Table 1. Argon isotopic ratio in two old feldspars

Sample no.	K-Content (%)	Age from A^{40}/K^{40} ratio in cogenetic biotite (billion years)	Ion intensity ratio extrapolated to time of admission of the sample to the mass spectrometer			Expected from GERLING <i>et al.</i> constants
			$A^{40}/(36 \text{ peak}) \times 10^{-4}$	$A^{40}/(38 \text{ peak}) \times 10^{-4}$	$(A^{40}/A^{38}) \times 10^{-4}$	$A^{40}/A^{38} \times 10^{-4}$
KA 24*	11.1	2.3	1.35 ± 0.08	6.0 ± 0.4	>70	4.3
KA 82†	11.2	2.4	5.6 ± 0.3	18.5 ± 2.5	>270	4.3

* From Yellow Medicine County, Minnesota.

† From Koochiching County, Minnesota.

70 and 270×10^4 , respectively, could be set for the A^{40}/A^{38} ratio. These results support those found by WASSERBURG and BIERI as contrasted to those given by GERLING *et al.*

We are indebted to Professor S. GOLDICH for the samples and the data on their K and A contents. We wish to thank Mr. R. OAKES for assistance with the measurements. The research was supported by the joint program of the U.S. Atomic Energy Commission and Office of Naval Research.

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REFERENCES

- GERLING E. K., LEVSKII L. K. and AFANAS'YEVA L. I. (1956) *Dokl. Akad. Nauk SSSR* **109**, No. 4, 813-815.
- WASSERBURG G. J. and BIERI R. (1958) *Geochim. et Cosmochim. Acta* **15**, 157-159.
- WASSERBURG G. J. and LIPSON J. (1958) *Cosmological and Geological Implications of Isotope Ratio Variations* p. 159. National Academy of Sciences-National Research Council, Publication 572.

Further comments on the vanadium-calcium coincidence at 3185 Å; reply to R. O. Scott and D. J. Swaine*

(Received 23 February 1959)

My note claimed no priority in finding the Ca line which coincides with V 3185 Å, but I acknowledge missing some references. I was principally concerned with making the coincidence more widely known to geochemists.

With regard to the study by Dr. SCOTT of the effect of extraneous elements on spectral line intensity, to which I referred, I see no reason to change my conclusions. In paragraph 3 of my note I was careful to avoid any reference to V 4379 Å: my remarks concerned V 3185 Å solely for which I still believe the so-called enhancement by calcium to be spurious.

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* Scott R. O. and Swain D. J. (1959) *Geochim. et Cosmochim. Acta* **16**, 195-196.

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- D. FLINN: An application of statistical analysis to petrochemical data
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